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EVALUATION OF SPARK SOURCE MASS SPECTROMETRY AND PLASMA EMISSION SPECTROSCOPY FOR COMPREHENSIVE ELEMENTAL ANALYSIS OF ENVIRONMENTAL SAMPLES

by

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Sample preparation, introduction, identification, and quantitation procedures were evaluated to gain an understanding of the elemental coverage and data quality to be expected using each technique.

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SECTION 1

INTRODUCTION

The complete and cost-effective elemental characterization of samples is a goal that has eluded analytical chemists. As quality control and environmental monitoring requirements become stricter and more comprehensive, the availability of a technique capable of supplying this information will be needed for analyses of both environmental and industrial samples. Only a few techniques can even be considered as candidates for this task. Those capable of multielemental analysis are inherently more desirable. Thus, classical colorimetric methods (Marczenko 1981) and atomic absorption spectrophotometry (AAS), while capable of providing acceptable accuracy and precision for many of the elements in the periodic table, in general cannot provide comprehensive simultaneous or near simultaneous multielemental data. The costs of obtaining a complete characterization of most samples by these methods are prohibitive.

X-ray fluorescence spectrometry (XRF) and proton-induced x-ray emission spectrometry (PIXE) (Khan and Crumpton 1981) have been shown to provide multielemental capability, but XRF suffers from high detection limits and the PIXE instrumentation is not available to most analysts.

Depending on the review consulted, instrumental neutron activation analysis (INAA) can determine from 20 to 70 elements in a single sample (Bowen 1980; Kovar 1984). However, two or more activation periods (the longest of which may be 30 days) may be required, as well as three to four different delay periods before final analysis. Lead (an environmentally significant element), most nonmetals, and all radioactive elements cannot be determined. Related nuclear techniques can be used to determine some of these elements, but in general, it is conceded that INAA and other nuclear techniques are not suitable for rapid comprehensive analysis. They are also seldom available to the analyst.

At present, only a few techniques have the potential for providing comprehensive elemental analysis in a cost-effective, timely manner. They are spark source mass spectrometry (SSMS) and the plasma emission spectrometric techniques involving inductively coupled (ICP) and direct-current (DCP) plasmas. This study evaluates existing work employing these techniques to determine if any are capable of providing comprehensive elemental screening of environmental samples and, if so, what limitations are to be expected.

Environmental samples are defined here to include all naturally present materials as well as substances introduced into the environment as solid, liquid, or gaseous wastes. These include geological materials such as soil, sediments, ores, and rocks; natural waters; energy and manufacturing process wastes including wastewaters, sludges, particulates, and feedstocks; and biological materials such as plants, blood, and urine. In general, manufactured products such as metal alloys, chemicals, pharmaceuticals, and other finished goods are not included.

Conclusions are summarized in Section 2. Specific objectives, the approach used, and the criteria for comparing the techniques are given in Section 3. Plasma techniques are discussed in Sections 4 and 5, and spark source mass spectrometry in Section 6. The techniques are compared in Section 7. Inductively coupled plasma-mass spectrometry (ICP-MS), a new technique, is reviewed in Section 8.

SECTION 2

CONCLUSIONS

2.1 ELEMENTAL COVERAGE

Neither ICP/DCP nor SSMS alone should be considered a comprehensive elemental analysis technique. Instead, ICP/DCP and SSMS should be considered complementary and not competitive techniques for achieving the goals of accurate, precise, and comprehensive elemental determinations. ICP is superior for determining a limited (~20) number of elements in a well-characterized matrix, provided spectral interference problems and sample preparation problems are understood and minimized. SSMS is capable of providing a semiquantitative screening analysis of any solid or liquid sample for more than 50 elements.

Very few studies have attempted to address the issue of comprehensive elemental analysis by ICP. Instead, studies have focused on a select group of elements of particular interest to the researcher. Many more elements have been successfully determined individually or in small groups by ICP/DCP than is possible in a single analysis. .

In general, ICP/DCP applications have addressed the determination of transition metals, alkaline metals, and alkaline earth metals. For these elements ICP/DCP systems appear to offer excellent coverage.

Based on the literature reviewed, ICP/DCP techniques currently are unsuitable for the routine analysis of nonmetals (with the exception of phosphorus and boron), and gaseous elements, including inert gases.

Determination of hydride-forming elements and mercury by ICP/DCP is not routine and is dependent on the availability of appropriate generating equipment that suitably interfaces with the plasma. The hydride generation process precludes determination of these elements with other elements. Determination of mercury by ICP offers no advantage over determination by cold-vapor atomic absorption.

Essentially, no data base exists for the determination of radioactive elements by ICP/DCP. A few studies have involved determination of uranium and thorium.

The ICP/DCP data base for precious metals and rare earth/lanthanide elements is small and inconclusive. These elements are generally present in intractable matrices that require tedious fusions, extractions, and separations. In the case of precious metals, the naturally low levels of these elements in environmental samples require preconcentration for detection by ICP/DCP spectrometer systems. Rare earths/lanthanide elements are almost always subject to severe spectral interferences due to major elements (Ca, Mg, Fe) that require a tedious cation resin separation from the rare earth elements (REE's). These time consuming, but apparently necessary, sample preparation procedures preclude the inclusion of rare earth and precious metal elements in a screening analysis involving a single sample.

2.2 SAMPLE PREPARATION PROCEDURES

Sample preparation procedures for ICP range from none in the case of a distilled-water matrix to complex fusions, extractions, preconcentrations, and acid digestions. Many of these procedures are custom designed to optimize for a select set of elements. In fact for many elements (hydride forming, REE's, precious metals) the sample preparation procedures are designed to remove other elements from the final solution to be analyzed. The design of an elemental analysis program involving determination by ICP spectrometer systems should consider carefully the potential interferences and detection-limit problems that a particular sample preparation scheme will entail.

The need for extensive sample preparation in SSMS is greatly reduced because of the technique's capability for direct analysis of solid samples. Particulate matter, ash, soil, rocks, or other inorganic solids generally do not require decomposition by using acids, fusions, or heat prior to their analysis. The key requirements that must be met are:

- The sample must form a stable electrode with the carbon or aluminum matrix.
- The organic content of the sample must be less than 50 percent.

Relatively high concentrations of organics produce significant spectral interferences on the photographic plate that make quantitation of the elements difficult. Levels >50 percent as carbon tend to interfere significantly.

Solids or liquids containing high (>50 percent) levels of organics generally are subjected to dissolution in a pressurized Parr acid (HNO_3) bomb. The resulting aqueous solution then is slurried with the graphite electrode material, the water is evaporated, and the electrode-sample mixture is analyzed by SSMS. Samples that are aqueous to begin with are treated similarly. Fusions are not required in SSMS because their objective is to free up an element or elements of interest from a refractory matrix that would otherwise not dissolve. The lack of need for sample dissolution for inorganics is a key advantage of SSMS over plasma techniques and other methods that require a liquid sample.

2.3 DATA QUALITY

Quoted detection limits for elements determined by ICP/DCP are almost always overly optimistic sometimes by a factor of 10 to 100. The detection limits for a single element in a distilled-water matrix always will be much lower than for the same element determined with other elements in a complex matrix.

Precision and accuracies that can be expected for aqueous solutions are on the order of 1 to 5 percent and 5 percent bias respectively. For samples requiring preparation, e.g., digestion or fusion, these are typically 20 percent RSD and 120 percent biased.

2.4 INTERFERENCES

Spectral interference compilations provided by manufacturers and available in open literature or in special publications (books) usually are not based on measurements made using an ICP or DCP system. The comparability of the information in these compilations to experimentally generated spectra is questionable and should be investigated further. There are so many emission lines available in the ICP/DCP plasma that most investigators use the line identification in the compilations without independent verification. No doubt this has resulted in the incorrect identification and quantitation of many elements by ICP/DCP.

2.5 OTHER

The marriage of the ICP source with a quadrupole mass spectrometer to form the hybrid technique ICP-MS appears to offer the potential for comprehensive low-interference measurements of environmental samples. However, the lack of adequate experience with the technique and the high cost of commercial instrumentation will probably restrict its impact for at least 5 to 10 years.

Marketing literature for ICP/DCP systems should be carefully scrutinized. Information presented regarding coverage of elements, detection limits and spectral interference correction capabilities are almost always idealized and may not apply to complex environmental samples.

The published data base for DCP spectrometer systems, very small by comparison to the relatively large data base available for ICP systems, is thought to be due to three factors. First, there are nearly a dozen manufacturers of ICP systems whereas only one company manufactures DCP systems. Second, it is generally considered that DCP systems offer poorer short-term precision (1 to 3 percent RSD) than ICP systems (<1 percent RSD). (Short-term precision is based on results of replicate analyses with very little time lapse between analyses (e.g., less than ½ day), whereas long-term precision is based on replicates across days, weeks, or longer). While this difference may not be of real significance in routine analysis, it is always used as basis for comparing the two systems. Finally, it has been reported that most DCP systems are used in industrial applications although it is not clear why this is so.

SECTION 3

STUDY DESIGN

3.1 OBJECTIVES

The Air and Energy Engineering Research Laboratory (AEERL) of the U.S. Environmental Protection Agency (EPA) at Research Triangle Park (RTP), North Carolina, for many years advocated the use of SSMS to perform comprehensive elemental survey analyses in its Level 1 (Lentzen et al. 1978; EPA 1979) environmental assessment studies. Such a comprehensive survey does not prejudge the significance of any one element or group of elements. Instead, as many elements as possible are determined so that even though health and environmental hazard levels may not now be available, when they are, the appropriate environmental data base will be available. In addition, for those elements for which hazard levels are known, the survey data can be used to define the scope of later studies. The goal of these assessment studies is to obtain data accurate to within a factor of 3 of the true value.

SSMS has successfully served the purpose of providing semiquantitative data for most elements to within a factor of three of the expected value where concentrations are known, as in analysis of National Bureau of Standards Standard Reference Materials (NBS-SRMs). The analytical precision of SSMS likewise has satisfied this goal. These conclusions have been confirmed by laboratory and data evaluations (Estes et al. 1979; Briden and Lewis 1981).

Until recently, no candidate technique was available to challenge SSMS in terms of cost per analysis, comprehensive elemental analysis capability, and data quality (accuracy, precision, detection limits). However, the recent development of commercially available plasma (ICP and DCP) emission spectrometers, the interest shown by other Agency laboratories in proposing plasma techniques as the chief elemental analysis techniques for environmental analyses, and the reported excellent accuracy and short-term/long-term precision of these techniques has prompted AEERL to reassess the role SSMS should play in analytical support work for the laboratory in Level 1 and related analysis activities.

The objectives of this study are to compare SSMS and the plasma techniques for the following characteristics:

- Elemental coverage or survey capability
- Ease of sample preparation
- Analysis time
- Interferences
- Accuracy
- Precision
- Detection limit
- Applicability to routine environmental analyses
- Availability of validated protocols
- Commercial availability.

The information generated from this assessment should prove useful in determining the future roles of SSMS and plasma techniques in AEERL-RTP sponsored programs.

3.2 APPROACH

The two principal sources used to form the information base for this evaluation were the scientific literature and recognized authorities and users of the techniques. Evaluating SSMS and plasma techniques posed some problems initially. Very little information concerning environmental analyses using SSMS has been published recently other than that produced by AEERL-RTP. On the other hand, plasma techniques have been the subject of hundreds of published articles in the past decade. A computerized search of Chemical Abstracts from the years 1975 to 1981 was conducted. The objectives described in Section 3.1 were used to define further the scope of the research. This search identified over 150 articles and books dealing with these areas. Approximately 130 of these were readily available and copies were obtained for review.

A list of journals known or thought to contain articles on plasma techniques was compiled and a search of these journals was conducted from

1975 through June 1983. Abstract listings and symposia proceedings were also surveyed. Discussions with technical experts from several of the plasma instrument manufacturers were held at the Short Course on Modern Emission Spectroscopy sponsored by the Society for Applied Spectroscopy in Philadelphia, September 1981.

3.3 COMPARISON CRITERIA

3.3.1 Technique Characteristics

A truly effective comparison of the capabilities of SSMS and plasma techniques would necessarily involve analyses of the same samples by both techniques. Because very little comparison data of this nature exists, a number of other characteristics that individually and collectively determine overall data quality must be evaluated. These characteristics are discussed in general in this section and in detail in subsequent sections.

The ability of a technique to determine large numbers of elements in a simultaneous or nearly simultaneous fashion in the same sample is defined here as its potential for comprehensive coverage. This coverage capability can provide qualitative, semiquantitative, or quantitative data. Each of these levels of specification will be evaluated.

The ease with which field samples can be processed prior to analysis is often a limiting factor as to (1) how long it will take to obtain the analytical result, (2) what fraction of the original matrix can be analyzed, and (3) what elements can be determined. Very complex matrices containing refractory forms of some elements often require elaborate sample dissolution/extraction steps that tend to be time consuming and restrictive as to the final number of determinable elements. These factors will be evaluated for both plasma spectroscopy and SSMS. Because no single sample preparation procedure exists, several of the most common will be evaluated.

Sample analysis, the part of analyte determination that begins with sample introduction into the measurement device and ends with data acquisition by a computer or other recording device, will be evaluated with respect to spectral interferences and sample transport. The advantages and disadvantages of various detector systems will be discussed.

Data processing is defined here as the handling of spectral data generated by the detector systems and recording devices.

Data quality will be evaluated by comparing plasma techniques and SSMS with respect to three common measures of method performance; accuracy, precision, and detection limit. Analyses of environmental samples of known composition will be the basis for the accuracy assessment. Precision will be assessed by comparing results obtained on repeat analyses of the same sample or on aliquots of the same sample taken through a sample preparation procedure. In the literature reviewed, detection limits seldom are evaluated for environmental matrices. Assessment of method detection limits is limited to a comparison of instrument manufacturer's claims, supplemented by suitable environmental data, if available.

The applicability of plasma and SSMS techniques to routine environmental analyses will be assessed by examining the availability of commercial instrumentation and analysis protocols as well as the relative and absolute costs of sample analysis on a per-element and per-sample basis.

3.3.2 Elements of Interest

In addition to determining which characteristics of SSMS and plasma techniques are most critical, the most probable list of elements for which analytical capability is needed must also be considered. Within EPA, this capability most likely will be based on the regulatory mandate of the environmental legislation which the Agency is funded to support.

Less than half of the 103 known elements are subject to regulation by EPA (Table 3-1). Of these 49 regulated elements, 19 are regulated only if they are radioactive. Methods capable of determining these 19 elements either individually or collectively already exist (Krieger and Whittaker 1980).

This leaves 31 nonradioactive elements for which there is a clear regulatory mandate. Most of these elements are subject to regulation under the Federal Water Pollution Control Act, the Resource Conservation and Recovery Act (RCRA), and the Superfund Act. This list includes, as a subset, all of the priority pollutant, drinking water standard, and RCRA/Extraction Procedure (EP) toxicity test elements. The nonregulated elements (Table 3-2) include gaseous elements, rare earths, noble metals, and some nonmetals.

TABLE 3-1. ELEMENTS REGULATED BY EPA

Element	CAA	FWPCA	SDWA	RCRA	TSCA	FIFRA	CERCLA	AEA	MPRSA
Nonradioactive									
Beryllium	X	X		X			X		
Boron							X[a]		
Fluorine	X	X	X				X		
Sodium		X		X			X		
Aluminum		X		X		X	X		
Phosphorus		X		X			X		
Sulfur		X					X		
Chlorine		X	X				X		
Potassium		X		X			X		
Calcium		X		X			X		
Vanadium		X		X			X		
Chromium		X	X	X			X		
Manganese		X	X						
Iron		X	X	X			X		
Cobalt		X					X		
Nickel		X		X			X		
Copper		X	X	X		X	X		
Zinc		X	X	X		X	X		
Arsenic	X	X	X	X		X	X		

See footnotes at end of table.

(continued)

TABLE 3-1 (continued)

Element	CAA	FWPCA	SDWA	RCRA	TSCA	FIFRA	CERCLA	AEA	MPRSA
Selenium		X	X	X			X		
Strontium	X	X		X			X	X	
Zirconium		X							
Silver		X	X	X			X		
Cadmium		X	X	X		X	X		X
Tin					X		X[a]		
Antimony		X		X	X	X	X		
Barium		X	X	X			X		
Mercury	X	X	X	X			X		X
Osmium				X			X		
Thallium		X		X			X		
Lead	X	X	X	X		X	X		
Radioactive									
Radon	X							X	
Iodine	X								
Cesium	X		X				X	X	
Radium	X		X				X	X	
Actinium	X		X				X	X	
Thorium	X		X						
Protactinium	X		X				X	X	
Uranium	X	X	X	X			X	X	
Neptunium	X		X				X	X	

See footnotes at end of table.

(continued)

TABLE 3-1 (continued)

Element	CAA	FWPCA	SDWA	RCRA	TSCA	FIFRA	CERCLA	AEA	MPRSA
Plutonium	X		X				X	X	
Americium	X		X				X	X	
Curium	X		X				X	X	
Berkelium	X		X				X	X	
Californium	X		X				X	X	
Einsteinium	X		X				X	X	
Fermium	X		X				X	X	
Mendelevium	X		X				X	X	
Nobelium	X		X				X	X	
Lawrencium	X		X						

CAA = Clean Air Act, 40 CFR 50-99.
FWPCA = Federal Water Pollution Control Act, 40 CFR 100-140.
SDWA = Safe Drinking Water Act, 40 CFR 141-149.
RCRA = Resource Conservation and Recovery Act, 40 CFR 240-399.
TSCA = Toxic Substances Control Act, 40 CFR 710-775.
FIFRA = Federal Insecticide, Fungicide and Rodenticide Act, 40 CFR 162-180.
CERCLA = Comprehensive Environmental Response, Compensation, and Liability Act (Superfund).
AEA = Atomic Energy Act, 40 CFR 190-211.
MPRSA = Marine Protection Research and Sanctuaries Act, 40 CFR 220-231.

[a] Not listed in regulations but analysis currently required by EPA.

TABLE 3-2. NONREGULATED ELEMENTS

Radioactive

Astatine
Francium
Technetium
Polonium
Promethium

Rare earth/ lanthanides

Lanthanum
Cerium
Praseodymium
Neodymium
Samarium
Europium
Gadolinium
Terbium
Dysprosium
Holmium
Erbium
Thulium
Ytterbium
Lutetium
Scandium
Yttrium

Noble metals

Iridium
Platinum
Gold
Palladium
Ruthenium
Rhodium

Metals

Lithium
Rubidium
Molybdenum
Indium
Tellurium
Hafnium
Tantalum
Tungsten
Rhenium
Bismuth
Magnesium
Silicon
Titanium
Gallium
Germanium
Niobium
Cesium

Nonmetals

Hydrogen
Helium
Oxygen
Neon
Krypton
Xenon
Argon
Carbon
Nitrogen
Bromine
Iodine

These elements seldom are considered significant environmental pollutants. For this reason, there are few programs within the Agency requiring their determination.

It is of some importance to note that AEERL-RTP for a number of years has collected environmental data from various types of pollution sources using SSMS. This data base has included some elements not specifically regulated by EPA. Often nonregulated elements are included in a sampling/analysis protocol because they are good tracer/indicator elements of other pollutants, (e.g., bromine in groundwater leachate from a landfill or magnesium as part of mass-balance considerations in a combustion process evaluation) because they may at some future date be subject to regulation, and because it is unlikely that additional opportunities to collect data on these elements will occur.

For these reasons, it is not the intention of this report to restrict the technique comparisons to the 31 elements shown in Table 3-1, although special attention will be given to these elements as a group. Instead, this review will examine the elements from several groupings that, it is hoped, will satisfy all potential users of these techniques for multielemental characterization of environmental samples. These categories include the following specific groups of elements whose similar properties and chemical behavior could permit simultaneous analysis:

- Radioactive elements
- Nonmetals
- Noble or precious metals
- Rare earths and lanthanides
- Volatile/hydride forming elements
- Alkali metals
- Alkaline earth metals
- Inert gases
- Transition metals.

For this discussion, the regulated and nonregulated elements have been combined and listed under these categories in Table 3-3.

TABLE 3-3. COMBINED REGULATED AND NONREGULATED ELEMENTS

Volatile/hydride-forming elements

- Germanium
- Arsenic
- Selenium
- Tin
- Antimony
- Mercury
- Tellurium
- Bismuth
- Lead

Alkali metals and alkaline earth metals

- Aluminum
- Silicon
- Lithium
- Sodium
- Magnesium
- Potassium
- Calcium
- Rubidium
- Strontium
- Cesium
- Barium

Radioactive elements

- Francium
- Radium
- Actinium
- Technetium
- Polonium
- Astatine
- Neptunium
- Uranium
- Thorium
- Protactinium
- Plutonium
- Americium
- Californium
- Berkelium
- Curium
- Einsteinium
- Fermium
- Mendelveium
- Nobelium
- Laurencium

Nonmetals

- Hydrogen
- Boron
- Carbon
- Nitrogen
- Oxygen
- Fluorine
- Sulfur
- Chlorine
- Phosphorous
- Bromine
- Iodine

Noble or precious metals

- Ruthenium
- Rhodium
- Palladium
- Silver
- Osmium
- Iridium
- Platinum
- Gold

Rare earths and lanthanides

- Cerium
- Praseodymium
- Neodymium
- Promethium
- Samarium
- Europium
- Gadolinium
- Terbium
- Dysprosium
- Holmium
- Erbium
- Thulium
- Ytterbium
- Lutetium

Transition metals

- Scandium
- Titanium
- Vanadium
- Chromium
- Manganese
- Iron
- Cobalt
- Nickel
- Copper
- Zinc
- Gallium
- Yttrium
- Zirconium
- Niobium
- Molybdenum
- Cadmium
- Indium
- Lanthanum
- Hafnium
- Tantalum
- Tungsten
- Rhenium

Inert gases

- Helium
- Neon
- Argon
- Krypton
- Xenon
- Radon

SECTION 4

PLASMA SPECTROSCOPY

The development of modern plasma spectroscopy generally is agreed to have originated in the independently published works of Greenfield et al. (1964) and Wendt and Fassell (1965). In the 1970's, these concepts were further developed into research instrumentation and later into commercially available plasma spectrometers. In the last 5 years, the field has seen its greatest growth with the availability of both simultaneous and sequential spectrometers for both routine and research analytical support. Since this review was begun in 1981, both the published literature and introduction of new commercial instrumentation have shown that the technique still is evolving rapidly. The applications of plasma spectroscopy to a wide variety of analyses are the major areas of interest today. The availability of more advanced data handling capabilities, availability of novel sample introduction techniques for gases and solids, and the potential for hybridization of the plasma with other detectors such as gas chromatography and mass spectrometry all indicate that the technique is becoming more useful to a wider variety of users than when first introduced. The increasing number of citations of plasma spectroscopy in the literature is also an indicator of growth in the technique's popularity. This section will provide a description of the plasma source, the sample preparation and introduction approaches that are most commonly employed, and the element detection and data processing systems that provide the results from the plasma analysis. Elemental coverage, data quality, and availability of standard operating procedures for plasma spectroscopy will also be discussed.

4.1 TYPES OF PLASMAS

A plasma is an electrically neutral luminous gas composed of free electrons, positively charged ions, and neutral atoms, which is more than 1 percent ionized. The gas is a stream of argon or argon/nitrogen that is ionized by the influence of a strong electric field generated by a radiofrequency (field induced) or by a direct current (Kahn et al. 1979a; Zander 1981). The temperatures experienced by a sample introduced into the plasma approach 5,000 to 10,000 K and result in the desolvation, decomposition, atomization, and ionization of the sample constituents. The complex atomic or ionic line emission spectra that are produced can be dispersed by a grating spectrometer and the emission line intensities measured by photomultiplier tubes or other types of detectors. The photocurrents thus generated then can be processed by a microcomputer system into concentrations for individual elements in the sample. The combination of plasma source, sample introduction system, spectrometer, detector, and data processor is known as a plasma emission spectrometer.

There are three types of field-induced plasmas:

- Inductively coupled (ICP) at radio frequencies (RF)
- Capacitively coupled at RF and/or microwave frequencies (CCP)
- Microwave induced plasmas (MIP).

Of these, only the ICP has gained commercial acceptance in the analysis of samples for elements. The CCP and MIP will not be discussed further.

There are two types of plasmas that can be produced by the discharge between two or more electrodes:

- Plasma jet or direct current plasma--a noncurrent-carrying electrode
- Plasma arc--current carrying electrode.

Of these, only the DCP has gained commercial acceptance.

The inductively coupled plasma and the direct current plasma are by far the most popular emission sources in plasma emission spectroscopy. The ICP is discussed in this section. DCP is discussed in Section 5.

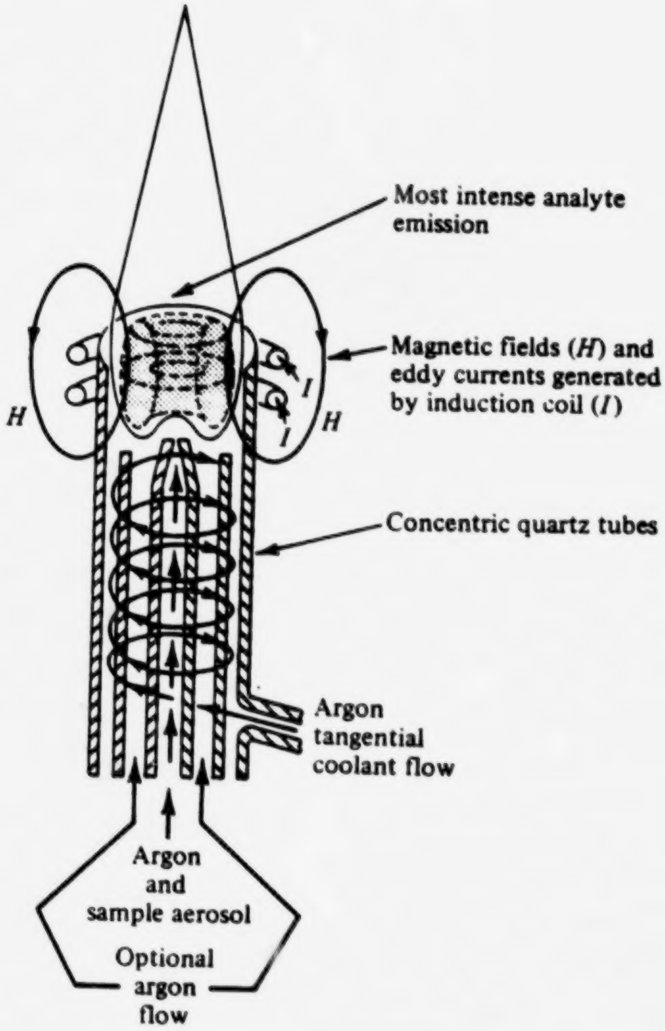
4.2 OPERATING PRINCIPLES OF INDUCTIVELY COUPLED PLASMAS

The ICP source consists of a radiofrequency (RF) generator and a series of concentric quartz tubes, called a torch, through which an inert gas is passed and ionized by means of induction coils powered by the RF generator. The most commonly used gas is argon. For this reason, the term inductively coupled argon plasma or ICAP is frequently used synonymously with ICP. Although there have been some investigations into the use of pure nitrogen gas or mixtures of nitrogen and argon as the ICP gas, all commercial instruments and nearly all users of the technique employ 100-percent argon. Although somewhat expensive, it is chemically inert and produces a high-temperature plasma.

A schematic of an ICP torch is shown in Figure 4-1. The water-cooled induction or load coils are wrapped around the top of the torch assembly and are connected to an RF generator operating at frequencies around 30 MHz producing a power of 1 to 5 kW. Three quartz tubes each carry a different stream of argon gas and have unique purposes in the generation and stabilization of the plasma (Kniseley et al. 1973; Boumans 1979). The plasma is generated by "seeding" the argon gas flowing through the tubes with electrons by means of a graphite load or a Tesla coil. The electromagnetic energy carried in the induction coil then couples with the electrons in the gas creating an inductively coupled plasma with temperatures around 10,000 K.

The oscillating magnetic field generates eddy currents in the plasma that flow in closed circles perpendicular to the coil axis. The resistance to this flow results in the heating of the argon to produce the plasma (Scott et al. 1974).

The gas stream used to initiate the plasma flows between the central and second tubes at around 0.5 to 1 L/min. (Set-ups for analysis of aqueous samples use the coolant gas flow to light the plasma.) This stream is sometimes called the auxiliary or intermediate gas flow. A second gas stream is introduced tangentially around the plasma gas stream through the outer tube at 10 to 15 L/min. This outer or coolant gas flows in a helical pattern up the outer tube and modifies the shape of the plasma tail plume into a toroidal or annular configuration. This gas flow also keeps the plasma from melting the outer tube. At the same time, the auxiliary gas flow lifts the plasma away from the walls of the middle and outer tubes. The third tube is used to carry the aerosolized sample into the core of the plasma.


Most intense analyte emission
Magnetic fields (H) and eddy currents generated by induction coil (I)
H
H
I
I
Concentric quartz tubes
Argon tangential coolant flow
Argon and sample aerosol
Optional argon flow

From: H. H. Willard, L. L. Merritt, Jr., J. A. Dean, and F. A. Settle, Jr., Instrumental Methods of Analysis, Sixth Edition, © 1981 by Litton Educational Publishing, Inc. Used by permission of Wadsworth, Inc.

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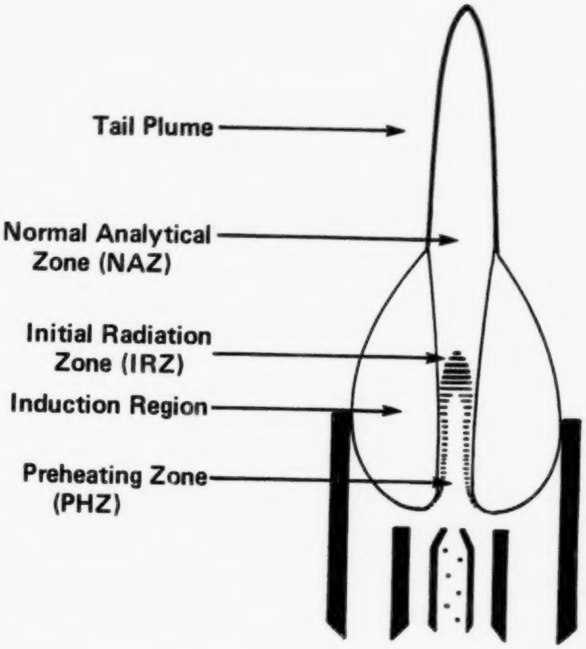
Figure 4-1. Schematic of an inductively coupled plasma torch.

The toroidal or doughnut shape of the plasma causes the axial region of the plasma to be cooler than the outer regions and facilitates introduction of the sample, which is injected at an argon flow rate of around 0.5 to 1.5 L/min through the central tube.

At the plasma temperature of around 10,000 K, the sample aerosol is desolvated, decomposed, and atomized producing a tail flame that is viewed by the spectrometer-detector system for the characteristic emission lines of interest. Because the plasma is spatially complex, the ideal location for viewing a particular element's emission lines will vary from element to element. By convention, the distance from the top of the load coil to the location of the emission line(s) within the plasma tail plume is termed the observation height. Some investigators (Koirtyohann et al. 1980) have proposed a different nomenclature based on properties of the plasma rather than external engineering reference points for comparing plasma regions. Although this approach to plasma nomenclature has not been accepted widely, the plasma schematic shown in Figure 4-2 is a useful description of the emission structure of the plasma and helps to explain why the ICP is an excellent emission source. The argon is highly ionized in the induction region, where most of the energy transfer from the load coil occurs. The high spectral background continuum of this region makes it of no analytical usefulness. Likewise, decreasing temperatures, entrainment of air, and increased molecular emissions from air molecules occur in the tail plume region. The normal analytical zone, the region in which all analytically useful emission measurements are made, falls just under the base of the tail plume afterglow and just above the apex of the plasma core (Willard et al. 1981).

Because the analytical zone is spatially resolved from most of the spectral background, the detection limits for elements are improved substantially over that of classical optical spectroscopic techniques. In addition, the small radius of the analytical zone results in a high emission of analyte atoms per unit of surface area (Greenfield 1976). Introducing the sample vertically through the center of the plasma minimizes the potential for self-absorption of the emission by cooler ions or atoms at the edge of the source. This results in a linearity of emission response over 5 to 6


Tail Plume
Normal Analytical Zone (NAZ)
Initial Radiation Zone (IRZ)
Induction Region
Preheating Zone (PHZ)

Reprinted with permission from S. R. Koirtyohann, J. S. Jones, and D. A. Yates, 1980, Nomenclature System for the Low-Power Argon Inductively Coupled Plasma, Analytical Chemistry 52:1965-1966. © 1980 American Chemical Society.

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Figure 4-2. Suggested nomenclature for the cross-sectional view of a toroidal ICP.

orders of magnitude of concentration (generally 50 µg/L to 500 mg/L in a liquid sample) (Ward 1984) and means that a single wavelength can be used to quantify over a wide range of concentrations.

The temperatures within the plasma result in the complete breakdown of all chemical compounds such that matrix effects are virtually nonexistent. The high temperatures also mean that ion line emission is far more likely than atom line emission. This is significant in the selection of emission wavelengths for identification and quantitation and requires that a comprehensive compilation of emission line spectra be available to the analyst.

As noted earlier, there are alternative torch designs and gas choices that offer advantages to the analyst. Although torch sizes vary somewhat depending on the manufacturer, most are in the range of 18 mm o.d. Alternative designs primarily seek to replace Ar, which is somewhat expensive, with N_2 or water or to reduce Ar consumption by constructing a smaller torch operating on less power.

The original plasma design of Greenfield (1976) used N_2 as the coolant gas and Ar as the other gases. To sustain such a plasma requires much more power, up to 5 kW, than does a 100-percent Ar plasma. Nitrogen plasmas generally have fallen into disfavor as all current commercial instrumentation use 100-percent Ar for all gas streams. Barnes and Meyer (1980) and Montaser and Montazavi (1980) have described the development of modern N_2/Ar plasma torches that operate at much lower input power, around 1 kW.

A second approach involves replacing the argon coolant gas stream with a water-cooled jacket. Kornblum et al. (1979), employed such a coolant stream, which reduced the Ar requirement to 2 L/min. Kawaguchi (1980) employed a similar system. Although both reported that detection limits did not deteriorate and that other characteristics of the plasma were not affected adversely, no commercial interest in this design has been shown.

A final approach to reducing both Ar and power consumption is simply to reduce each in a standard 18 mm o.d. torch (Montaser et al. 1981) and/or to reduce the size of the torch o.d. from 18 mm to 13 mm (Savage and Hieftje 1979) or to 9 mm (Allemand et al. 1979; Weiss et al. 1981) with accompanying reduction in Ar and power requirements. Although these designs have not gained commercial acceptance, the development of a mobile ICP spectroscopy system would seem to depend on such alternative designs being available.

4.3 SAMPLE PREPARATION PROCEDURES

4.3.1 Overview of Procedures

This section and Section 7.2 will address the advantages and disadvantages of procedures used to prepare samples for analysis by SSMS and ICP/DCP-atomic-emission spectrometry (AES) methods. Considerations will include the sample matrix, impact on coverage of elements and impact on data quality, including detection limit, precision, accuracy, and representativeness of the processed sample.

The preparation of samples for analysis in SSMS and ICP/DCP-AES methods may involve many similar intermediate steps but ultimately will result in the analysis of a solid by SSMS and a liquid by ICP/DCP-AES. There is a growing body of evidence that suggests that direct analysis of solids by ICP/DCP-AES is feasible, but in general, conventional ICP/DCP-AES sample introduction systems will only accept liquids or vapors.

Despite the apparent vast difference in objectives for SSMS and ICP/DCP-AES sample preparation, the goals of sample preparation can be stated in a form applicable to both classes of techniques.

- Sample Homogenization - This involves the generation of a representative aliquot of the original sample for analysis and of any subsequent preparations that may be required.
- Sample Dissolution or Decomposition - This is the most common form of pretreatment and involves changing the raw sample into a form compatible with the sample introduction system of the analytical instrument.
- Sample Preconcentration - This increases the concentration of target elements to detectable and quantifiable levels.
- Sample Separation - This is required to remove potential interferring substances from the sample matrix. The interference may be of a spectral or chemical nature or both.

There is often no clearcut distinction among the above categories since their specific procedures typically are used in common with each other as part of the overall process. Many procedures can be considered to address several goals simultaneously. It therefore will be almost impossible to present examples from one category without involving those from another.

The best sample preparation procedure is none at all. However, this course of action is seldom available or advisable in the case of environmental samples. Even the best procedure or combination of procedures will be subject to one or more of the following limitations. The selection and design of a sample preparation scheme should consider the impact of these limitations on the overall analysis goals.

1. Increased detection limit - Because most sample preparation methods ultimately will result in dilution of the original sample matrix and its constituents of interest, the effect is to raise the detectable level of a target element when referenced back to the original sample. For example, if Cd is present in a sample at 10 µg/g (10 ppm) and the sample preparation procedure calls for dissolution of 1 g of sample, which is brought to a final volume of 100 mL, the effective concentration of Cd in the analyzed liquid can be no greater than 100 µg/L (0.1 ppm). Hence, the detection limit for Cd has been raised by a factor of 100 for this sample.

2. Incomplete sample dissolution - This is a common problem even when combinations of acids, fusions, heat and pressure are used. The significance of the undissolved material will depend on the analysis goals, the anticipated coverage of elements and the composition of the undissolved fraction. Most analysts tend to ignore this aspect because they are interested in solubilizing only a limited number of elements.

3. Sample contamination - The use of reagents, decomposition vessels, and the necessity of sample transfers all contribute to the possible contamination of the sample. In general, the more difficult the matrix is to solubilize and the greater the coverage of elements that is desired, the greater the likelihood of sample contamination.

4. Loss of elements by volatilization, coprecipitation - The sample preparation process may cause certain elements to be driven off as volatile gases or compounds, reducing the potential coverage of elements by the detection process. Arsenic, selenium, antimony, mercury, boron, silicon, and lead often are lost from the sample by this process. Other elements may be lost by coprecipitation with insoluble matrix and reagent materials.

5. Time commitment - The complexity of multielement sample preparation methods makes them inherently time-consuming and labor-intensive. Again the coverage required and the matrix will dictate the number and complexity of steps required.

6. Coverage of elements.

It is almost impossible to design a sample preparation scheme without at least one of the above limitations creating significant problems.

Sample preparation procedures that have been used in conjunction with SSMS and ICP/DCP analyses are given in Table 4-1.

4.3.1.1 Decomposition Methods--

Both inorganic and organic (primarily biological) materials constitute environmental samples. Decomposition of these matrices prior to analysis mainly has involved the use of acids in open systems or bombs, fusions, and thermal treatment in muffle furnaces. Practically every combination of these methods has been explored. Advantages and disadvantages of procedures for decomposition of inorganic matrices have been reviewed by Sulcek et al. (1977). Those procedures that have been used to prepare samples for ICP/DCP analysis are discussed here. The decomposition of a solid is defined by them "to be a series of reactions which transform the original substance and produce quantitatively new phases. The reactions are generally accompanied by the formation of gaseous phases."

4.3.1.2 Decomposition in Bombs--

A very popular sample preparation procedure that has been used for both inorganic and organic matrices is the pressure decomposition of a sample in a heated, closed vessel. The pressure increases due to the increasing temperature. At higher temperatures and pressures, the activity of mineral acids (H_2SO_4, HCl, HNO_3, $HClO_4$, HF) are increased along with the dissolution rates of the sample materials.

Most bombs consist of a Teflon (polytetrafluoroethylene) insert, which contains the sample, and a steel cylinder which encloses the Teflon vessel. Inserts composed of Pt, Pt alloys, Au, polycarbonate and polypropylene have been used. The well-known Parr Bomb is an example of a bomb with a Teflon insert.

TABLE 4-1. SPECIFIC CLASSES OF SAMPLE PREPARATION PROCEDURES

Homogenization

1. None
2. Grinding
3. Sieving
4. Shaking
5. Compositing

Decomposition

1. None
2. Acids
    a. In open systems
    b. In closed systems (bombs)
3. Fusion
4. Thermal decomposition
5. Plasma decomposition
6. Combinations of the above

Preconcentration

1. None
2. Resin sorption
3. Coprecipitation
4. Chelating agents
5. Freeze drying
6. Evaporation
7. Volatilization
8. Extraction
9. Fusion

Separations

1. Same as under dissolution
2. Same as under preconcentration

The success of a bomb-dissolution procedure over an open-system decomposition cannot be predicted, because it is the choice of acids, other pretreatments employed (such as preashing in a muffle furnace), and the sample matrix which determine the eventual success of the decomposition. The bomb merely accelerates the process. Bomb dissolutions also tend to retain elements such as Ge, As, B, Si, and Hg that form volatile species during decomposition and reaction with acids that would be lost in an open system. Problems with bomb decompositions include corrosion of the metal portion of the bomb and distortion of the insert after prolonged exposure to acids and pressure. The metal corrosion may become severe enough to contaminate the sample. Unusual levels of Fe, Cr, and Ni in the decomposed sample along with obvious signs of corrosion of the steel cylinder are signs of potential bomb-induced sample contamination.

4.3.1.3 Decomposition in Open Systems with Acids

Inorganic acids used in the decomposition of samples include volatile acids (HCl, HNO_3, and aqua regia), less volatile acids ($HClO_4$, H_2SO_4, and H_3PO_4), and HF.

Hydrofluoric acid (HF) is a weak acid that decomposes inorganic materials by complexing elements with fluoride. It is the only acid that reacts with silicon, silicon dioxide, and silicates, forming the water-soluble compound H_2SiF_6. In the process, the cationic compounds present in the silicate matrix are released. When heated, H_2SiF_6 decomposes to form the volatile SiH_4.

Because it decomposes silicon compounds, HF cannot be used or stored in glass vessels. Teflon is the best choice as a reaction or storage vessel for it. Generally, 38- to 40-percent HF is used. HF may also produce other volatile compounds, including GeF_4, SiF_4, SnF_4, TiF_4, ZnF_4, AsF_3, AsF_5, SbF_3, SbF_5, NbF_5, and BF_3. Conditions must be optimized to prevent these elements from boiling off. The opposite also tends to occur: some fluoride compounds are precipitated. These precipitates, which are usually not soluble in other acids, often can be resolubilized by adding boric acid, H_3BO_3, although there are no guarantees.

Whereas decomposition with HF is often needed in preparing samples for plasma analyses, it seldom is required for SSMS. HF also damages the glass parts of the ICP-AES sample delivery system and torch assembly. This has prompted manufacturers to offer HF-resistant torches, nebulizers, and spray chambers composed of aluminum compounds.

Hydrochloric acid, a slight reducing agent and a strong acid, is the most frequently used reagent in the decomposition of inorganic matrices. It dissolves the original solid-phase material, converts fusion melts into soluble salts, and also dissolves natural and synthetic carbonates.

Nitric acid is a strong acid and a powerful oxidizing agent used alone or in combination with other acids for oxidative dissolution of polyvalent elements in minerals or organics. Both anionic and cationic components are oxidized during reaction with HNO_3. Reaction products are the gases NO and NO_2. Mixtures of nitric and perchloric acids are used to oxidize organic components in sedimentary rocks. Nitric acid can be evaporated from the sample digest by heating although in the presence of sulfuric acid--a less volatile acid--nitrosylsulfuric acid is formed that is difficult to evaporate.

A mixture of 3:1 v/v concentrated HCl and HNO_3 forms the powerful oxidant aqua regia (AR), which can solubilize platinum group elements.

Perchloric acid ($HClO_4$) exhibits its oxidizing properties only in hot concentrated solutions, especially in conjunction with nitric acid. Hot $HClO_4$ reacts explosively with organic substances except Teflon. $HClO_4$ has been used in combination with HF to decompose rocks and coal.

Sulfuric acid is a weak oxidant, but a powerful dehydrating agent, and is more effective when combined with other acids. Sulfur dioxide is a product of the decomposition process when sulfuric acid is used.

Phosphoric acid, H_3PO_4, combines the dehydrating properties of H_2SO_4 and the complexing properties of HF, but has no oxidizing properties. It displaces volatile inorganic acids from their salts. Insoluble phosphates are formed when H_3PO_4 is used.

4.3.1.4 Decomposition by Fusion--

Fusions are used to decompose sample matrices in which the elements of interest are present in an acid-insoluble matrix, generally silicate or aluminosilicate in nature. A fusion agent, either an alkaline carbonate, hydroxide, peroxide, or alkaline borate, is added in considerable excess to the sample and heated together to a high temperature in a Pt, Ni, Zr, or C crucible. The materials melt together and the original matrix materials form a homogeneous mixture with the fusion material (sometimes called flux), which can be dissolved in acid and analyzed for elements. Fusions are often the only way to solubilize otherwise intractable matrices. Disadvantages include the necessity of using fusion material in great excess of the sample, contamination of the sample with impurities present in the fusion agent, and corrosion of the crucible walls by the alkaline flux. The contaminants introduced into the fused sample often prevent determination of trace elements in the original sample. The resulting high concentrations of Na, K, or B in the final sample may interfere with spectroscopic determination of elements.

There are three types of fusions. Alkaline fusions involve fusion with carbonates, hydroxides, peroxides, and borates. Alkaline fusions are used most frequently and will be described in more detail. Acidic fusions with pyrosulfates, hydrofluorides, fluoroborates, and basic oxide and oxidizing-reducing fusions with alkaline fusion agents mixed with oxidants or reductants are employed less commonly.

Sodium and potassium carbonates are the most frequently used alkaline fusion agents. They melt at 800 to 1,000 °C. The fusion-melts partly dissociate, forming corrosive oxides. Corrosion can be suppressed by fusing under a CO_2 atmosphere. Pt or Pt-alloy crucibles are used most often for carbonate fusions. Alloying with Ir or Rh improves the mechanical strength of Pt, while addition of Au (5 percent) or Zr (0.1 percent) increases the chemical resistance of the crucible. Pt is corroded not only by the sodium oxide produced by the thermal decomposition of sodium carbonate during fusion, but also by reaction with ferrous compounds present in the melt. The Pt-Fe alloy formed during fusion is difficult to remove from the crucible even with concentrated HCl. In addition, the iron will cause iron determinations to be biased high. Also the iron is oxidized to ferric oxide during fusing and segregates along the boundaries between the Pt crystals. This causes embrittlement and eventual crumbling of the crucible (Saylor et al. 1979).

Sodium carbonate is most frequently used in fusion of silicate materials. An acid-soluble, alkaline mono- or disilicate is formed in the reaction with silicon dioxide. Aluminum from aluminosilicates partially are converted into aluminate and form some acid-soluble carbonates. Most silicate materials can be decomposed by sodium carbonate. The completeness of the reaction is a function of the grain size of the material and the duration and temperature of the fusion. Silicates rich in aluminum, beryl, zircon, and titanite are decomposed poorly. Because carbonate fusion is oxidative, corrosion of the crucible is likely. Complete volatilization of As, Se, Tl, and Hg occurs during carbonate fusion. Work carried out by McGrath (1984) confirms this for As in SRM 1633a.

Alkali hydroxides (NaOH and KOH) are used as fusion agents. Corrosion of the crucible is reduced if the fusion is carried out in an inert atmosphere. At least a 10-fold excess of NaOH or KOH to sample is needed and may be applied as an aqueous or alcoholic solution that is evaporated to dryness after application to the sample. The melt is often observed creeping up the crucible walls. Losses of Hg, Se, Tl, Re, and Te are common.

Sodium peroxide, the most effective alkaline fusion agent, has numerous disadvantages. Commercially available Na_2O is often too impure to use. Corrosion of the crucible is also a major problem. Zirconium crucibles are more resistant to corrosion (losing 5 mg Zr/g of fusion agent) than are Ag or Ni crucibles (losing 100 to 200 mg/g of Na_2O). Explosion of vapors above the fusion flux is possible if organics or other easily oxidizable substances are present.

The most popular nonoxidizing fusion agents are the alkali meta- and tetraborates. The anhydrous salts are used after dehydration at 700 to 800 °C. A 95/5-percent Pt/Au alloy is not wetted by the tetraborate melt, and is therefore easier to pour out the melt. Tetraborates are efficient fusion agents for oxygen-containing minerals of Al, Ti, Fe, Sn, Ta, and Nb. Alkali metal tetraborates often are employed for sample preparation for x-ray fluorescence. The popularity of this application has led to the development and availability of automatic fusion systems, such as the Claisse Fluxer, that can simultaneously prepare six samples in Pt-Au alloy crucibles using sodium tetraborate or lithium metaborate. Lithium metaborate is a more efficient fusion agent than sodium tetraborate and requires an oxidizing atmosphere. Fusion agents generally require repurification before use in trace element determinations.

Sintering is sometimes used in place of fusions to reduce contamination, crucible corrosion, and concentrations of Na or K in the final melt. A much lower excess of sintering agent is used (1- to 2-fold excess) than in fusions, and a lower temperature is used. Whereas fusions generally take 10 to 15 min, sintering may require 30 to 180 min.

4.3.1.5 Sample Separation and Concentration Methods--

Bachmann (1981) has reviewed multielement separation and concentration methods for trace elements. Concentration can be relative or absolute. Absolute concentration procedures result in a decrease in sample mass via extraction or evaporation, whereas relative procedures increase the ratio of trace to major elements as in selective resin sorption, in which the objective is to completely separate trace elements from major elements. Separation methods can be classified according to procedures for separating the trace elements of interest, the matrix elements, or specific interferring elements. These include dry- and wet-ashing and freeze-drying procedures.

Extraction procedures include treatment with chelating agents, ion associating agents, and other agents that result in direct extraction of the elements of interest. Parameters that can be varied or must be controlled to effect the extraction include pH, the use of organic solvents, and other ions. Chelating agents are used to selectively complex transition and platinum-group metals, leaving behind alkali and alkaline earths, which do not form complexes with these agents and are generally present as major components. Examples of commonly used chelating agents include APDC (ammonium pyrrolidine dithiocarbamate), oxine (8-hydroxyquinoline), PAN(1-[2-pyridylazo]-2-naphthol), and dithizone (diphenylthiocarbazone). These work by complexing with the metals of interest in aqueous solution. The organometallic complex is then extracted into a smaller volume of organic solvent such as MIBK (methyl isobutyl ketone), chloroform, benzene, or carbon tetrachloride. The solvent is reduced in volume by evaporation and the remaining solvent is analyzed. Contamination, loss of sample, or loss of elements of interest by adsorption onto container walls or by volatilization often are problems and may offset any improvement in detection limits in the original sample.

Sorption methods generally result in either adsorption or ion exchange of the trace elements or matrix elements onto or into a resin. Depending on the process used, the trace elements can be desorbed and determined or the sorbent can be incinerated or digested and the elements determined in the residue. Batch, column adsorption, and impregnated filters have been used. Dowex ion-exchange resins with carboxyl and sulfoxyl functional groups can be used to separate selectively and preconcentrate lanthanides, actinides, and transition metals. Alkali and alkaline earths are generally matrix elements and are not sorbed as easily onto or into resins. The selectivity of the sorption process is often improved by varying the pH of the system.

Evaporation and volatilization methods include wet and dry ashing, evaporation of liquids, and hydride generation by volatilization from liquids. Generation of volatile metal chelates by GC has been used for some ICP-AES applications. Coprecipitation and matrix precipitation also have been used to separate elements of interest from a matrix.

Bachmann (1981) makes an important point regarding the choice of concentration method to be used in conjunction with a specific detection method. Concentration methods that result in significant contamination of the sample should not be combined with extremely sensitive detection methods and vice versa. The analyst must be aware of the limitations of both the sample preparation and detection (analysis) methods.

The concentration methods that have received ICP-AES applications have included extractions of complexes into organic solvents (the effect of organics on the plasma is described in the applications discussions), precipitation and coprecipitation requiring several additional steps to dissolve the precipitate, resin sorption, and volatilization of hydride forming elements from aqueous solution.

The choice of a multielement analysis concentration method should be based on:

- Matrix elements and major constituents
- Elements to be determined
- Concentration of the trace elements
- Sample form and amount of sample

- Accuracy and precision requirements
- Time necessary for the concentration
- Detection methods which are available.

4.3.2 Sample Preconcentration and Separation Methods Used in ICP-AES

In some matrices the concentrations of certain elements are at or below the detection/quantitation limits of the measurement method. A preconcentration may be required to determine these elements. Likewise, if elements that prevent determination of the elements of interest are present in the sample, they must be removed prior to measurement. Both of these sample preparation procedures tend to reduce the coverage of elements in a single sample. Certainly those elements that must be removed as interferences, as well as to increase the number of subsamples that must be analyzed to meet the analysis goals, clearly are concerns that must be considered for plasma methods as indicated in the following examples.

Barnes and Genna (1979) and Mahanti and Barnes (1983a, 1983b) have developed an elemental preconcentration/separation procedure using a polydithiocarbamate resin to complex metals prior to ICP-AES determination of the elements of interest. The resin is not available commercially and must be synthesized by the user. Samples that have been acid-digested or otherwise solubilized in water are passed through the resin column. Because complexation of metals by the resin is highly pH-dependent, the coverage of elements in a single sample passed through the resin column is limited. The resin must be digested in a mixture of nitric and sulfuric acids prior to ICP-AES determination.

Barnes and Genna (1979) reported on the determination by ICP-AES of 10 elements in urine collected on this resin. The resin procedure was used to separate the elements of interest from major elements (alkali and alkaline earths, Ca, Mg) present in urine that can contribute to excessive spectral background shifts and stray-light interferences. These major elements do not complex with the resin and thus are not present in the digested resin solution. The use of the resin also resulted in a 125-fold concentration of the elements of interest (250 mL of urine passed through the resin resulting in 2 mL of digested resin solution) and as a result, lower detection limits than for a similar acid matrix not subjected to resin preconcentration (Table 4-2). The number of elements determinable in a single urine sample was, as previously noted, pH-dependent.

Element	pH
Sn, Se	1
Hg, Cu, Cd, Pb	5
U	6
Ni, Bi, Te	not given

Clearly the determination of these ten elements would require at least five separate analyses. The authors used a sequential ICP-AES for detection.

Mahanti and Barnes (1983a) determined certain trace elements in coal, fuel oil, and shale oil by ICP-AES after preconcentration on this resin. The coal (NBS SRM 1632a) was dried for 2 h at 100 °C. Digestion of 1-g samples in a PTFE bomb with concentrated HF/HNO_3 (2 mL/15 mL) for 10 h at 150 °C was found to be unsatisfactory, resulting in incomplete dissolution of the sample. Dissolution was achieved by first ashing in a muffle furnace (1 g for 2 h at 275 °C; 4 to 5 h at 500 °C) followed by PTFE bomb dissolution with HF/AR (2 mL/10 mL) for 2 h. The bombed coal was brought to a final volume of 100 mL.

NBS SRM 1634a residual fuel oil and TOSCO shale were digested with 25 mL concentrated HNO_3/6 mL perchloric acid on a hot plate at 200 °C and evaporated to near dryness. This was repeated until the sample appeared to be completely digested. It was then brought to 70 mL with deionized water.

Again, resin complexation was found to be pH-dependent:

Element	pH
Cu, Fe, Mo, Ti, V, Ni, Co, Pb	5
U, Th	6
Ce, La	8
Mn, Zn	9

A different volume of sample solution (10 to 100 mL) was required for each determination, and pH had to be adjusted by using a unique procedure for each set of elements and matrix. The instrumental operating conditions and the pH requirements of the resin complexation process would seem to

TABLE 4-2. DETECTION LIMITS[a] (μg/L) FOR STANDARDS PREPARED IN DISTILLED WATER, 60 PERCENT V/V (VOLUME PER VOLUME) NITRIC ACID-SULFURIC ACID MIXTURE, AND URINE

Element	Wavelength (nm)	Distilled water	Acid matrix[c]	Urine[b]
As	193.76	80	100	0.8
Bi	289.80	20	30	0.2
Cd	226.50	2	5	0.04
Cu	324.75	2	6	0.05
Hg	253.65	200	400	3
Ni	341.48	2	7	0.06
Pb	405.78	30	40	0.3
Sb	217.58	100	200	1.6
Se	196.09	30	40	0.3
Sn	303.41	200	500	4.0
Te	238.58	20	50	0.4
U	385.96	20	40	0.3

[a] Detection limit is the concentration equivalent to two times the standard deviation of the background signal.

[b] Calculated for 125 × concentration factor.

[c] Detection limits in acid matrix greater than in water due to greater viscosity of acid resulting in decreased aspiration rate compared to water.

Source: Barnes and Genna (1979)

increase greatly the number of successive measurements required to characterize the same original sample. Even though detection limits were 12 to 60 times lower for concentrations of elements in coal as a result of resin pretreatment (oil detection limit improvement not given) (Table 4-3) and results for analyses of SRMs were acceptable (Tables 4-4, 4-5, and 4-6), the need to vary the forward power of the ICP and to use a separate aliquot of resin digest or original sample material for pH adjustment reduces considerably the simultaneous/sequential coverage of elements (Table 4-7). To determine 13 elements in a single sample required at least 6 separate analyses.

Mahanti and Barnes (1983b) determined six elements in high-purity graphite after first ashing the graphite in a muffle furnace at 800 °C for 12 h, dissolving the ash in aqua regia, adjusting the pH, and passing the digest through a polydithiocarbamate resin (Cu, Fe, Si, Ti, V) or an acrylamidoxime resin (Al). Sample pH was adjusted prior to resin separation: pH 5 (Fe, Ti, V); pH 8 (Si); pH 6 (Al). Neither resin complexes with B or group 1A or 2A elements (Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra). It was not clear that enough solution was obtained from the final resin digest (5mL) to permit determination of Cu, Fe, Si, V, Ti in the same original sample. Levels found ranged from 0.1 to 0.5 μg/g.

4.3.3 Sample Decomposition Methods Used in ICP-AES

4.3.3.1 Coal and Fly Ash--

The determination of elements in coal and fly ash is important in evaluating combustion-process and related control-device efficiencies as well as in assessing mass balance closure for a particular process. Because literature sample preparation procedures are meant to be general, not all elements typically are addressed in a single protocol. Coal preparation methods typically require oxidation of the coal prior to further decomposition steps whereas fly ash procedures presume that organics have been oxidized completely in the combustion process and therefore can be analyzed directly as in SSMS or solubilized in a digestion prior to ICP-AES analysis.

4.3.3.1.1 Comparison of methods--The most comprehensive evaluation of sample decomposition methods for coal and fly ash is that of McGrath

TABLE 4-3. DETECTION LIMITS AND OPERATING CONDITIONS FOR ELEMENTS IN COAL AND OIL SAMPLES USING RESIN PRECONCENTRATION

Element	Detection limit (μg/L)[a]	λ (nm)	Power (kW)
Ce	50	413.715	0.5
Co	10	345.35	0.5
Cu	5	324.754	0.8
La	8	408.67	0.5
Mn	2	257.61	0.7
Mo	8	202.03	0.7
Ni	10	341.48	0.5
Pb	150	220.35	0.7
Ti	4	333.94	0.7
Th	50	283.73	0.7
U	100	385.958	0.7
V	8	292.40	0.7
Zn	9	213.856	0.7

[a] Concentration giving a signal equal to 3 times the standard deviation of the background of an acid matrix. Observation height for all elements 16 mm above induction coil except for Pb, Th, U (14 mm).

Source: Mahanti and Barnes (1983a).

TABLE 4-4. RESULTS FOR ELEMENTS IN NBS SRM 1632a COAL

Element	Expected (μg/g)	Found (μg/g)[a]	% Bias	% RSD
Ce	30	29.7 ± 0.9	-1	3
Co	6.8	6.7 ± 0.1	-1	1
Cu	16.5 ± 1.0	16.3 ± 0.2	-1	1
Fe	1.11 ± 0.02%	1.10 ± 0.02%	-1	2
La	16	15.2 ± 0.8	-5	5
Mn	28 ± 2	27.1 ± 0.4	-3	1
Mo	--	5.7 ± 0.1	-	2
Ni	19.4 ± 1	19.6 ± 0.2	+1	1
Pb	12.4 ± 0.6	11.8 ± 0.2	-5	2
Th	4.5 ± 0.1	4.4 ± 0.1	-2	0
Ti	0.18%	0.170 ± 0.005%	-6	3
U	1.28 ± 0.02	1.3 ± 0.02	+2	2
V	44 ± 3	42 ± 2	-5	5
Zn	28 ± 3	28 ± 4	0	14

[a] Mean of 3 replicates ± SD.

TABLE 4-5. RESULTS FOR RESIDUAL FUEL OIL

Element	Expected µg/L	Found[a] µg/L	% Bias
Ce	--	<LOD	--
Co	0.3	0.28 ± 0.006	-7
Fe	31	30.8 ± 0.4	-1
La	--	<LOD	--
Mn	0.19 ± 0.02	0.18 ± 0.004	-5
Mo	0.12	0.11 ± 0.003	-8
Ni	29 ± 1	29.2 ± 0.5	+1
Pb	2.8 ± 0.08	2.68 ± 0.03	-4
Th	--	<LOD	--
U	--	<LOD	--
V	56 ± 2	55.5 ± 1	-1
Zn	2.7 ± 0.2	2.54 ± 0.03	-6

LOD = Limit of detection.

[a] Mean of 3 replicates ± SD.

TABLE 4-6. RESULTS FOR SHALE OIL

Element	Sample weight (g)	Weight of element (μg)			Recovery (%)
		Added	Expected	Found	
Ce	1	2	2	1.95 ± 0.05	97.5
Co	3	1	1.3	1.25 ± 0.02	96.2
Cu	2	1	2.22	2.20 ± 0.03	99.1
Fe	0.2	5	14.14	14.0 ± 0.2	99.0
La	1	2	2	1.96 ± 0.04	98.0
Mn	1	1	1.9	1.89 ± 0.03	99.5
Mo	1	1	1.58	1.53 ± 0.03	96.8
Ni	2	1	2.26	2.20 ± 0.04	97.3
Th	1	2	2	1.98 ± 0.04	99.0
U	1	2	2	1.95 ± 0.05	97.5
V	1	1	1.51	1.48 ± 0.03	96.8
Zn	1	4	12.06	12.0 ± 0.15	99.5

TABLE 4-7. MATRIX OF CONDITIONS TO DETERMINE TRACE ELEMENTS IN COAL BY RESIN PRECONCENTRATION

pH	Power		
	0.8 kW	0.5 kW	0.7 kW
5	Cu, Fe	Co, Ni	Mo, Ti, V
6	--	--	Pb, U, Th
8	--	Ce, La	--
9	--	--	Mn, Zn

(1984). The primary objective of this study was to evaluate the effectiveness of various readily available preparative and analytical techniques in the determination of major and minor elements in samples associated with combustion processes including coal and fly ash. The samples analyzed were NBS SRM 1632a bituminous coal, NBS SRM 1633a coal fly ash, and several coal and fly ash samples from in-house combustion studies. The prepared samples were analyzed by both atomic absorption spectrophotometry (AAS) and inductively coupled argon plasma emission spectrometry. In addition, NBS SRM 1632 coal and NBS SRM 1633 fly ash were analyzed for elements by SSMS. The AAS results are not relevant to the ICP-AES vs. SSMS comparison and will not be considered further. The sample preparation procedures are summarized in Table 4-8 and Figures 4-3 and 4-4. A select set of elements was determined in each sample using a Jarrell-Ash Model 855 Atom Comp ICAP Spectrometer. This is a direct reader equipped with separate channels for each element emission line. The elements for which channels were available on this instrument are listed in Table 4-9 along with the emission line wavelength and the detection limit in aqueous solution. The instrument initially was standardized using five mixed-element calibration standards containing 10 μg/mL of the individual analytes in 2- to 3-percent acid. After calibration, the emission from each sample was measured in three consecutive 10-s integrations. Certain of the digestates were pumped into the nebulizer by means of a peristaltic pump at the desired 2 mL/min flow rate rather than by direct instrumental aspiration. This was implemented primarily for the high "salts" digestate matrices. Appropriate background and interelement corrections were applied by the instrument's computer software and the elemental concentrations were printed out on a Texas Instruments Silent 733 Electronic Printer interfaced to a PDP 8A minicomputer.

SSMS sample electrode preparation procedures and operating parameters were as follows.

Sample electrodes for the analysis of Parr oxygen bomb combustates of coal samples were prepared in the following way:

- Combustate solution was placed in a vycor dish and mixed with an internal standard (10 μL of 100 μg/mL In) and approximately 300 mg of graphite.
- This mixture was slurried and dried under an infra-red (IR) lamp.

TABLE 4-8. COAL AND FLY ASH SAMPLE PREPARATION METHODS EVALUATED

Method	Summary	Reference
High-temperature muffle furnace ashing	Used for coal only in this study. Sample dried to constant weight in desiccator and heated in porcelain crucible in muffle furnace first to 300 °C; then to 500 °C; held at 500 °C (2 h); removed; sitrred; returned to furnace; heated at 750 °C until constant weight achieved.	Standard Test Method--ANSI/ASTM D3682-78
Low temperature ashing (LTA)	Used for coal only in this study. LFE Model LTA-302(a) Low Temperature (<300 °C) asher. An oxygen stream activated by radio frequency energy is passed over sample; gaseous byproducts of reaction removed by vacuum. Coal (1 g) predried spread thinly, in tared quartz boats (to obtain efficient ashing) subjectd to RF power of 250 W at chamber pressure of 1.1 mg Hg and oxygen flow rate of 9.2 cc/min for 4 h. Samples removed stirred and the LTA process continued until constant weight achieved.	
Lithium metaborate fusion	Used for coal samples previously ashed in muffle furnace or LTA and for fly ash without prior preparation. Ash (0.1 g) weighed into 15 mL Pt crucible, mixed with 0.5 g $LiBO_4$, 0.5 g $LiBO_4$ added on top of mixture. Heated in muffle furnace at 1000 °C for 15 min until visibly fused. Cooled at ambient temperature; outside of crucible rinsed with deionized water, -crucible placed in clean TFE fluorocarbon beaker with 5 percent (HCl (150 mL) and warmed for 30 min until fusion melt solubilized. Crucible and contents rinsed with 5 percent HCl into 200 mL volumetric flash along with beaker and contents.	ASTM D3682-78
Aqua regia digestion	Coal ash (1.0 g) or fly ash (1.0 g) refluxed (6 h) in flask with 48 mL concentrated Ultrex HNO_3/12 mL Ultrex HCl (aqua regia). Condenser rinsed into distillation flash. Flask contents filtered through Whatman #41 filter paper and brought to 100 mL in volumetric flask.	Lentzen et al. 1978

(continued)

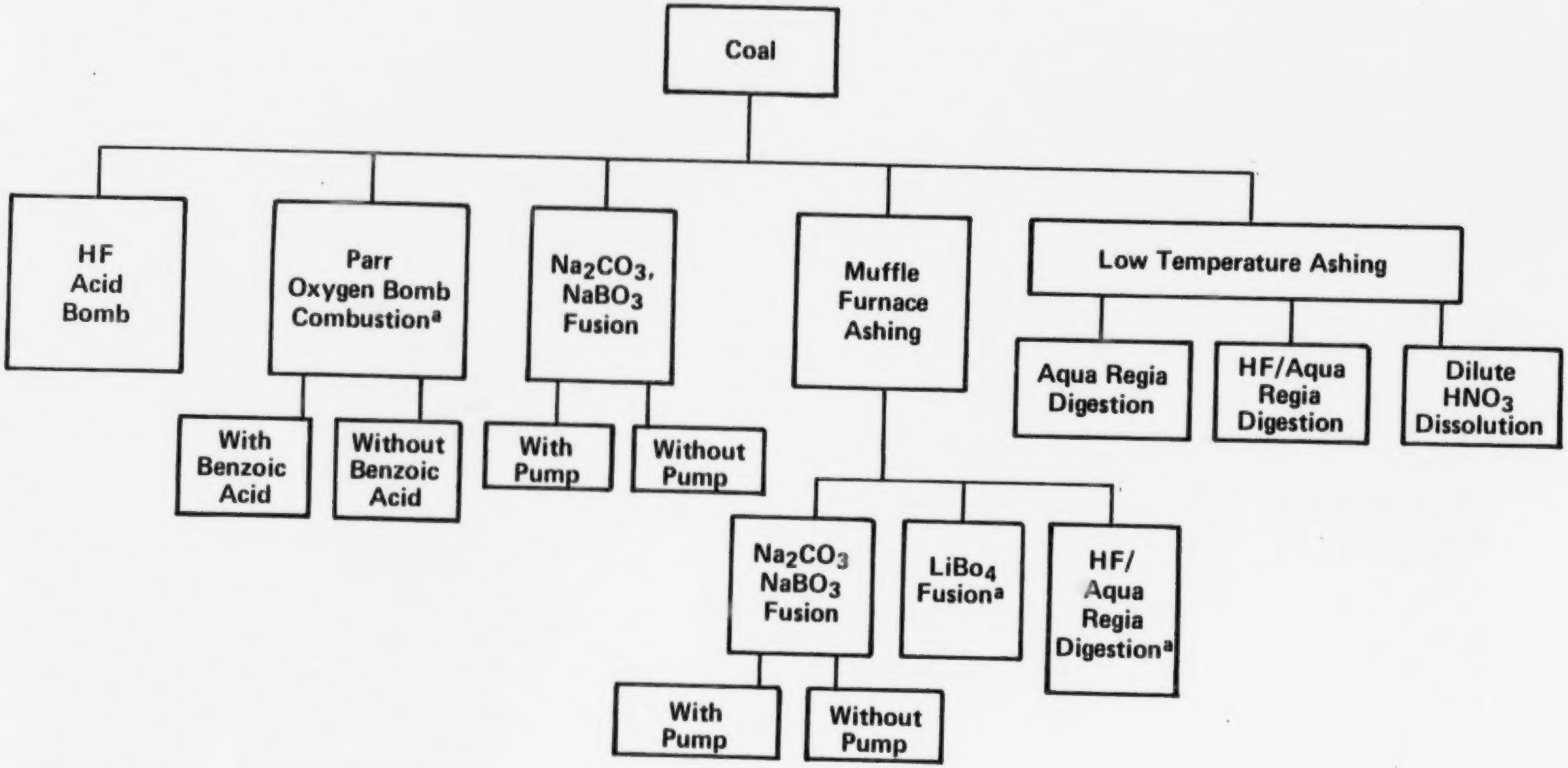
TABLE 4-8 (continued)

Method	Summary	Reference
Hydrofluoric acid/ aqua regia digestion	Coal ash or fly ash (0.2 g) reacted with 3 mL aqua regia, 5 mL HF in a screw capped Teflon tape sealed 125 mL Nalgene bottle in a water bath at 80 °C for 2 h. Saturated boric acid (50 mL) added to the extract. Cooled sample adjusted to 100 mL volume.	Standard Test Method ANSI(ASTM D3683-78
Parr oxygen bomb combustion	For those samples prepared by the Level 1 procedure, approximately 1 g of coal was mixed with 0.25 g benzoic acid. The admix was then pelletized and placed in a precleaned vycor crucible. Those samples prepared according to the ASTM D3684-78 Method were directly aliquotted (1 g) into the crucible. The sample/benzoic acid pellet or sample and crucible were subsequently placed in the electrode support of the bomb over 10 mL of 10 percent Ultrex nitric acid. The platinum fuse wire was adjusted to contact the coal sample and the bomb assembled. Slowly charged with oxygen to a pressure of 30 atm, placed in a water bath, ignited, allowed to cool in the water bath, for 10 min, and slowly depressurized. The contents and bomb washings of all surfaces were quantitatively transferred to a 100-mL volumetric flash and bought to volume.	Lentzen et al. 1978
Sodium carbonate/ sodium borate fusion	An aliquot of the coal or fly ash, 1 g, was placed in a 15 mL platinum crucible and mixed with 5 g of 3:1 sodium carbonate/ sodium borate. The crucible was placed in a cold muffle furnace and brought to 750 °C. It was maintained at this temperature until the fusion was complete, approximately 15 min. The crucible was removed from the furnace, allowed to cool, and placed in a beaker. Fifty mL of 50 percent HCl was added and the beaker warmed until complete dissolution of the melt. The solution was allowed to cool, quantitatively transferred to a 100-mL volumetric flask, and the beaker and crucible successively rinsed with deionized water. The volumetric was then brought to final volume.	Perkin-Elmer 1973

(continued)

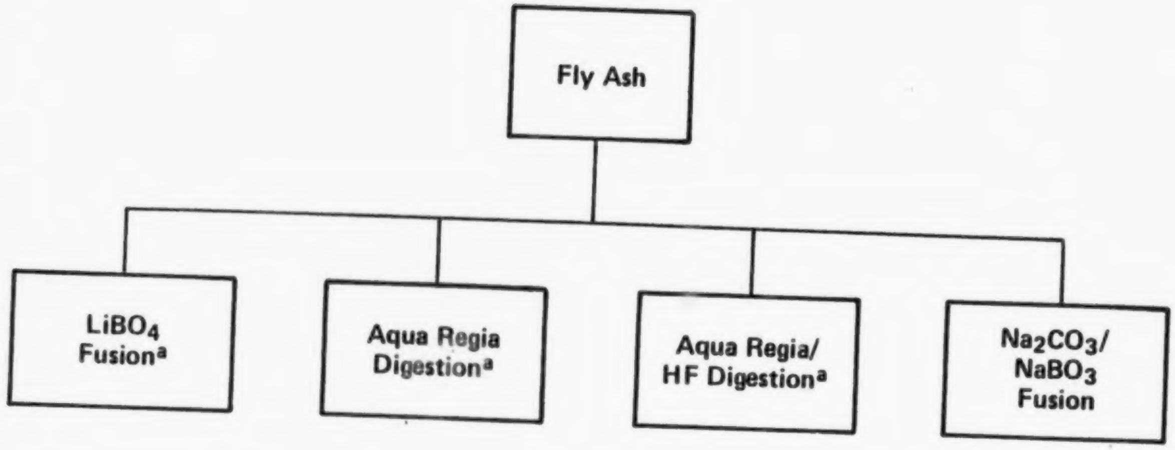
TABLE 4-8 (continued)

Method	Summary	Reference
Hydrofluoric acid bomb	An aliquot of coal, approximately 0.5 g, was weighed into the Teflon sample cup. Six mL of concentrated nitric acid was added, the bomb sealed and heated for 2.5 h in an oven at 150 °C. It was then allowed to cool and 3 mL concentrated HF added. The bomb was resealed and again heated at 150 °C for an additional 15 min. The sample and bomb rinsings were subsequently transferred to a 50-mL volumetric flask containing 2.8 g of boric acid. The boric acid crystals were solubilized, the sample homogenized and transferred to a nalgene bottle. The digestate was refrigerated until analysis.	Hartstein et al. 1973
Dilute nitric acid dissolution	Coal and coal fly ash samples carried through the low temperature ashing procedure were solubilized from the quartz boat by the addition of 5 mL concentrated Ultrex HNO_2. The boat was gently warmed until total dissolution of the ash was achieved. The solubilized ash was then quantitatively transferred to a 50-mL volumetric and brought to volume.	-


Coal
HF Acid Bomb
Parr Oxygen Bomb Combustion[a]
With Benzoic Acid
Without Benzoic Acid
Na_2CO_3, $NaBO_3$ Fusion
With Pump
Without Pump
Muffle Furnace Ashing
Na_2CO_3 $NaBO_3$ Fusion
With Pump
Without Pump
$LiBo_4$ Fusion[a]
HF/ Aqua Regia Digestion[a]
Low Temperature Ashing
Aqua Regia Digestion
HF/Aqua Regia Digestion
Dilute HNO_3 Dissolution

[a]Also applied to real world coal samples.

Figure 4-3. NBS-SRM 1632a coal sample preparation procedures prior to ICP-AES analysis.


Fly Ash
$LiBO_4$ Fusion[a]
Aqua Regia Digestion[a]
Aqua Regia/ HF Digestion[a]
Na_2CO_3/ $NaBO_3$ Fusion

[a]Also applied to real world fly ash samples.

Figure 4-4. NBS SRM 1633a fly ash sample preparation procedures prior to ICP-AES analysis.

TABLE 4-9. INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY WAVELENGTHS AND AQUEOUS DETECTION LIMITS

Element	λ (nm)	Detection limits (μg/L)[a]
Al	308.2	9
As	197.2	30
Ba	493.4	1
Be	234.8	1
Cd	228.8	1
Co	228.6	3
Cr	205.5	3
Cu	324.7	2
Fe	259.9	4
Mn	257.6	1
Mo	202.0	2
Ni	231.6	5
Pb	220.3	20
Sb	206.8	20
Se	196.0	20
Ti	334.9	1
V	292.4	5
Zn	213.8	1

[a] Detection limits for aqueous standards.

Source: McGrath (1984)

- After repeating the slurrying process, the dried mixture was placed in an agate container and further homogenized with a Spex mixer mill for 30 min.
- The homogenous mixture then was packed into polyethylene slugs and pressed into electrodes under 10 to 11 ton/in. pressure.

Fly ash sample electrodes were prepared by initially slurrying a weighed aliquot (0.1 g) with deionized water and 0.150 g of Spex graphite. The slurry was subsequently spiked with 10 µL of 1,000 µg/mL In as the internal standard. The procedure described above then was implemented beginning with the first dry down of the slurry under the IR lamp.

For analysis, the sample electrodes were mounted in the ion source of the mass spectrometer JEOL Analytical Instruments Inc. (Model JMS-01BM-2 Mass Spectrograph) where they were "sparked" by a high-voltage discharge that decomposed and ionized the electrode mixture. The positively charged ions were accelerated and the ion beam formed was energy-focused and momentum-dispersed for collection on an ion-sensitive photoplate. Instrumental standard operating parameters utilized for these analyses are:

Pulse repetition rate (Hz)	1,000
Pulse length (µs)	40
Magnet Current (A)	4.00
Accelerating voltage (kV)	28.4
Analyzer Pressure (torr)	4×10^{-9}
Source Pressure (torr)	$\sim 1 \times 10^{-7}$

Based on recoveries, precision, matrix interferences, and mechanical or manipulative difficulties, it was determined that no single preparative or analytical technique could be applied to the quantitative analysis of coal or fly ash to determine adequately all of the major or minor elements studied. SSMS came closest to providing the optimal coverage of elements with the least sample preparation required but the accuracy and precision of the results were poor. Certain preparation methods favored either major or minor elements. Table 4-10 gives the methods of choice for preparation and analysis of coal and fly ash samples with respect to recoveries and precision on an element-by-element basis. ICP-AES was found to provide just as acceptable data as AAS and was determined to be the analytical

TABLE 4-10. PREPARATIVE METHODS OF CHOICE FOR THE DETERMINATION OF MAJOR AND MINOR ELEMENT CONSTITUENTS IN COAL AND COAL FLY ASH BY ICP-AES

Element	Preparative method	
	Coal	Fly ash
Al	HF/AR	LMB
As	None	HF/AR
Ba	SCSB	LMB
Be	ND	None
Cd	HF/AR/LTA	None
Co	HF/AR	HF/AR
Cr	LMB: HF/AR:SCSB	LMB
Cu	HF/AR: HF bomb	None
Fe	LMB: HF/AR	LMB
Mn	LMB: PB: HF/AR/LTA	LMB
Mo	None	None
Ni	HF/AR: HF bomb	LMB: HF/AR
Pb	None	None
Sb	None	None
Se	None	None
Ti	LMB: HF/AR	LMB
V	LMB: HF/AR	LMB
Zn	HF/AR	LMB

HF/AR = Hydrofluoric acid/aqua regia digestion
LMB = Lithium metaborate fusion
: = or
/ = and
PB = Parr oxygen bomb combustion (coal only)
SCSB = Sodium carbonate/sodium borate
LTA = Low temperature plasma ashed
ND = Not determined, no expected value available

method of choice due to its simultaneous analysis capability. As indicated in this table, no method was acceptable for Pb, Sb, Se, and Mo in either coal or fly ash, nor was any method acceptable for As in coal and Be, Cd, and Cu in fly ash. Al extracted with Pb suppressed the intensity of the ICP-AES Pb channel. With a sequential spectrometer this could be avoided. Even for those elements for which acceptable preparative procedures were identified, there is little overlap indicating once again that the sample preparation procedures and not the ICP analytical method dictate the coverage of elements. Lithium metaborate fusion (LMB) was the method of choice for 9 of 18 elements in fly ash while HF/AR digestion after muffle-furnace ashing was the method of choice for 8 of 18 elements in coal.

Discussion of Results

Lithium metaborate fusion of muffle-furnace ashed coal and unashed fly ash (Table 4-11 and 4-12) suffered from high levels of Cu and Pb in the $LiBO_4$, equivalent to 200 to 250 µg/g in coal and 1,000 to 1,100 µg/g in the fly ash. These levels were approximately 10 times greater than the Cu and Pb levels in the coal and fly ash. In addition Co (6 µg/g), Ni (20 µg/g), and Zn (180 µg/g) were present at significant levels in the metaborate. This illustrates the significance of contamination from reagents in sample preparation. Recoveries of Zn and Ba were less than 75 percent in coal with precision of Zn and Ba greater than 25 percent RSD. Recoveries and precision data for As, Cd, Mo, Pb, Sb, and Se were not presented for coal, primarily because the ICP-measured concentrations in solution were below the instrumental detection limits.

Recoveries of Al, Co, Cr, Fe, Mn, Ni, Ti, and V in coal and for Al, Ba, Co, Cr, Fe, Mn, Ni, Ti, V, and Zn in fly ash were between 75 to 120 percent. RSD's for all elements for which these were calculated were less than 25 percent except for Zn in coal and Cu in fly ash. Aqua regia digestion of fly ash and low-temperature ashed (LTA) coal recoveries generally were less than 70 percent for coal and less than 10 percent for fly ash with precisions <10 percent for all elements except As, Be, and Mo in fly ash (Tables 4-13 and 4-14). It can be concluded that this sample preparation method is unacceptable for these matrices. Part of the reason for these low recoveries is the evolution of nitrous oxide from the excess aqua

TABLE 4-11. ANALYSIS OF NBS COAL FLY ASH SRM 1633a BY LITHIUM METABORATE FUSION - QUANTITATION BY ICP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	140,000	134,000	96	5
As	145	<60	--	--
Ba	1,500	1,260	84	5
Be	12	36.4	303	6
Cd	1.0	<2	--	--
Co	46	51	111	8
Cr	196	168	86	5
Cu	118	685	580	32
Fe	94,000	90,300	96	5
Mn	190	149	78	5
Mo	29	<4	--	--
Ni	127	97.7	77	11
Pb	72.4	NG	--	--
Sb	7	<40	--	--
Se	10.3	<40	--	--
Ti	8,000	8,490	106	5
V	300	278	93	6
Zn	220	244	111	16

[a] Represents mean of six determinations.

NG = Blank value is higher than sample.

TABLE 4-12. ANALYSIS OF NBS MUFFLE FURNACE ASHED COAL SRM 1632a BY LITHIUM METABORATE FUSION - QUANTITATION BY ICP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	30,700	23,900	78	10
As	9.3	<13	--	--
Ba	122	76.6	63	30
Be	NR	3.4	--	3
Cd	0.17	--	--	--
Co	6.8	8.2	120	5
Cr	34.4	31.9	93	16
Cu	16.5	NG		
Fe	11,100	9,740	88	12
Mn	28	24.5	88	0.03
Mo	NR	<0.9	--	--
Ni	19.4	13.7	71	17
Pb	12.4	NG	--	--
Sb	0.58	--	--	--
Se	2.6	<9	--	--
Ti	1,750	1,630	93	6
V	44	38.9	88	12
Zn	28	15.0	54	42

[a] Represents mean of five determinations.

NG = Blank value is higher than sample.
NR = Not reported.

TABLE 4-13. ANALYSIS OF NBS COAL SRM 1632a BY AQUA REGIA METHOD (LEVEL 1 PROCEDURE) OF LOW TEMPERATURE PLASMA ASHED COAL - QUANTITATION BY ICP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	30,700	6,695	22	0.1
As	9.3	<3	--	--
Ba	122	40.9	34	1.7
Be	NR	2.5		4.7
Cd	0.17	0.11	66	4.5
Co	6.8	4.9	71	6.1
Cr	34.4	13.0	38	1.5
Cu	16.5	6.1	37	6.6
Fe	11,100	7,420	67	4.2
Mn	28	17.0	61	6.5
Mo	NR	<0.2	--	--
Ni	19.4	12.7	65	0
Pb	12.4	<3	--	--
Sb	0.58	<3	--	--
Se	2.6	<3	--	--
Ti	1,750	151	9	1.9
V	44	20.4	46	2.9
Zn	28	17.2	61	3.5

[a] Represents mean of two determinations.

NR = Not reported.

TABLE 4-14. ANALYSIS OF NBS COAL FLY ASH SRM 1633a BY AQUA REGIA METHOD (LEVEL 1 PROCEDURE) - QUANTITATION BY ICP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}$[a]		
Al	14,000	1,150	0.8	1.6
As	145	2.1	1.4	48
Ba	1,500	36.8	2.4	1.2
Be	12	0.6	5.3	22
Cd	1.0	<0.1	--	--
Co	46	1.0	2.2	4.5
Cr	196	1.9	1.0	5.3
Cu	118	1.7	1.4	7.7
Fe	94,000	2,710	2.9	1.6
Mn	190	2.8	1.5	4.5
Mo	29	0.4	1.4	25
Ni	127	2.6	2.1	3.8
Pb	72.4	<2	--	--
Sb	7	<2	--	--
Se	10.3	<2	--	--
Ti	8,000	59.1	0.7	1.8
V	300	4.4	1.5	3
Zn	220	4.6	2.1	4.3

[a] Represents mean of two determinations.

[b] Not certified.

regia. It caused problems in the direct aspiration of samples into the ICP-AES. Matrix matching of calibration standards and samples as well as pumping of samples into the ICP did not resolve this problem.

The HF/AR digestion procedure was found to have serious sample manipulation problems including degradation of the ICP torch by residual HF and potential analyst exposure hazard due to bulging of the reaction bottle caused by evolution of gases during the sample digestion. Analyses of coal ashed by muffle furnace and LTA procedures, carried through this procedure, gave recoveries that were essentially the same, with recoveries for 10 of 18 elements within 75 to 125 percent (Tables 4-15 and 4-16). Results for fly ash were somewhat poorer with acceptable recoveries for 7 of 18 elements (Table 4-17).

The Parr oxygen bomb combustion method was evaluated by bombing coal samples directly and by pelletizing them with benzoic acid. Neither variation resulted in acceptable recoveries or precisions (Tables 4-18 and 4-19).

Sodium carbonate/sodium borate fusion of coal was evaluated for muffle-furnace ashed and unashed coal and for fly ash. Ashing resulted in lower recoveries for Al, Ba, Cr, Fe, Mn, and V (Tables 4-20 through 4-23). In general, this procedure provided much better recoveries for major elements such as Al, Fe, Co, Cr, Mn, and Ti than for minor constituents. This is due partly to the high blank levels observed for the minor elements As, Cu, Ni, Pb, Zn, and Sb. Hydrolysis of the fusion melt was also a problem although it is not clear if addition of acid to the melt could not prevent this. The use of a pump to aid sample transport into the ICP had no significant impact on the results.

Hydrofluoric acid bombing should retain more volatile elements as well as release constituents bound as silicates. For this study it did not recover volatile elements from unashed coal, As, Se, Sb, or Pb very well and for other elements Cr, Cu, Ni, and Zn the precision was poor (Table 4-24). Residual HF also degraded the ICP torch.

Direct HNO_3 solubilization of low-temperature ashed coal gave good recoveries for Cd, Co, Cu, Fe, Mn, and Ni and poor recoveries for all other elements evaluated (Table 4-25).

TABLE 4-15. ANALYSIS OF NBS COAL SRM 1632a. EXTRACTION BY HYDROFLUORIC ACID/AQUA REGIA OF MUFFLE FURNACE ASHED COAL - QUANTITATION BY ICP

Element	Concentration (μg/g) Expected	Concentration (μg/g) $\bar{X}^a$	Mean % recovery	% RSD
Al	30,700	26,100	85	4.0
As	9.3	NG	--	--
Ba	122	818	670	176
Be	--	5.2	--	24
Cd	0.17	0.15	88	47
Co	6.8	7.2	106	7.4
Cr	34.4	29.3	85	7.8
Cu	16.5	14.9	90	16
Fe	11,100	94,000	85	1.0
Mn	28	17.0	61	68
Mo	--	NG	--	--
Ni	19.4	15.1	78	17
Pb	12.4	<2	<18	0
Sb	0.58	3.0	525	50
Se	2.6	<2	<85	2.3
Ti	1,750	1,640	94	1.5
V	44	40.3	92	4.0
Zn	28	23.4	84	6.8

[a] Represents mean of seven determinations.

NG = Blank value is higher than sample.

TABLE 4-16. ANALYSIS OF NBS COAL SRM 1632a. EXTRACTION BY HYDROFLUORIC ACID/AQUA REGIA OF LOW TEMPERATURE ASHED COAL - QUANTITATION BY ICP

Element	Concentration (μg/g)		Average % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	30,700	31,700	103	2.4
As	9.3	<5	<49	0.2
Ba	122	399	327	62.9
Be	NR	7.7	--	1.6
Cd	0.17	<0.2	<89	0
Co	6.8	7.9	117	5.7
Cr	34.4	33.6	98	2.5
Cu	16.5	16.7	101	5.2
Fe	11,100	10,800	97	1.9
Mn	28	28.3	101	2.9
Mo	NR	<0.3	NG	--
Ni	19.4	16.3	84	2.3
Pb	12.4	<3	<24	--
Sb	0.58	<3	--	--
Se	2.6	<3	--	--
Ti	1,750	1,776	101	4.2
V	44	47.6	108	2.8
Zn	28	27.4	98	2.4

[a] Represents average of five determinations.

NG = Blank value is higher than sample.

NR = Not reported.

TABLE 4-17. ANALYSIS OF NBS COAL FLY ASH SRM 1633a. EXTRACTION BY HYDROFLUORIC ACID/AQUA REGIA. QUANTITATION BY ICP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	14,000	88,060	63	3
As	145	42.2	29	26
Ba	1,500	1,793	120	17
Be	12	57.5	480	1
Cd	1.0	<0.5	<50	--
Co	46	47.7	104	5
Cr	196	154	79	3
Cu	118	75.3	64	2.9
Fe	94,000	60,160	64	2.3
Mn	190	114	60	3.4
Mo	29	<1	<3	--
Ni	127	97	76	2.3
Pb	72.4	<10	<14	--
Sb	7	<10	--	--
Se	10.3	<10	<97	--
Ti	8,000	6,698	84	2.8
V	300	223	74	2.6
Zn	220	189	80	2

[a] Represents mean of five determinations.

TABLE 4-18. ANALYSIS OF NBS COAL SRM 1632a. PREPARED BY PARR OXYGEN BOMB COMBUSTION (NO BENZOIC ACID) - QUANTITATION BY ICP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	30,700	2,150	7	13
As	9.3	1.8	20	94
Ba	122	13.2	11	5
Be	NR	0.6	--	17
Cd	0.17	0.04	24	125
Co	6.8	4.4	65	41
Cr	34.4	82	238	77
Cu	16.5	39.2	238	43
Fe	11,100	1,590	14	140
Mn	28	30.6	109	29
Mo	NR	0.7	--	157
Ni	19.4	346	178	54
Pb	12.4	--	--	--
Sb	0.58	--	--	--
Se	2.6	--	--	--
Ti	1,750	156	9	27
V	44	10.7	24	28
Zn	28	35.7	128	17

[a] Represents mean of five determinations.

NR = Not reported.

TABLE 4-19. ANALYSIS OF NBS COAL 1632a. PREPARED BY PARR OXYGEN BOMB COMBUSTION (LEVEL 1) - QUANTITATION BY ICP

Element	Concentration (μg/g) Expected	$\bar{X}^a$	Mean % recovery	% RSD
Al	30,700	335	1	26
As	9.3	4.8	52	73
Ba	122	0.8	<1	50
Be	NR	0.1	--	0
Cd	0.17	0.19	112	95
Co	6.8	0.3	4	100
Cr	34.4	5.3	15	36
Cu	16.5	0.7	4	140
Fe	11,100	195	2	29
Mn	28	0.9	3	22
Mo	NR	1.4	--	157
Ni	19.4	0.8	4	100
Pb	12.4	1.4	11	171
Sb	0.58	1.0	172	220
Se	2.6	1.4	54	171
Ti	1,750	17.2	<1	21
V	44	2.9	7	28
Zn	28	4.2	15	36

[a] Represents average of six determinations.

NR = Not reported.

TABLE 4-20. ANALYSIS OF NBS COAL SRM 1632a BY SODIUM CARBONATE/SODIUM BORATE FUSION OF UNASHED COAL - QUANTITATION BY ICP, NO PUMP

Element	Concentration (µg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}$[a]		
Al	30,700	21,600	70	4.2
As	9.3	NG	--	--
Ba	122	105	86	4.7
Be	NR	6.10	--	2.1
Cd	0.17	0	0	0
Co	6.8	6.7	98	2.1
Cr	34.4	33.0	96	26
Cu	16.5	NG	--	--
Fe	11,100	8,460	76	4.3
Mn	28	22.5	80	9.3
Mo	NR	0	0	0
Ni	19.4	9.40	48	9.1
Pb	12.4	NG	--	--
Sb	0.58	NG	--	--
Se	2.6	<4	--	--
Ti	1,750	1,340	77	20
V	44	31.9	72	2.2
Zn	28	53.2	190	41

[a] Represents average of two determinations.

NR = Not reported.

NG = Blank value is higher than sample.

TABLE 4-21. ANALYSIS OF NBS COAL SRM 1632a BY SODIUM CARBONATE/SODIUM BORATE FUSION OF UNASHED COAL - QUANTITATION BY ICP, USING RAININ PUMP

Element	Concentration (μg/g)		Average % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	30,700	18,600	61	3.7
As	9.3	NG	--	--
Ba	122	84.3	69	4.4
Be	NR	4.32	--	5.6
Cd	0.17	<0.2	--	--
Co	6.8	7.9	104	5.6
Cr	34.4	40.5	118	24
Cu	16.5	NG	--	--
Fe	11,100	8,240	74	3.7
Mn	28	22.2	79	9.9
Mo	NR	NG	NG	NG
Ni	19.4	11.3	58	13
Pb	12.4	NG	--	--
Sb	0.58	NG	--	--
Se	2.6	<4.0	--	--
Ti	1,750	1,360	78	3.1
V	44	31.8	72	0.38
Zn	28	57.2	204	31

[a] Represents average of three determinations.

NG = Blank value is higher than sample.
NR = Not reported.

TABLE 4-22. ANALYSIS OF NBS COAL SRM 1632a BY SODIUM CARBONATE/SODIUM BORATE FUSION OF MUFFLE FURNACE ASHED COAL - QUANTITATION BY ICP, NO PUMP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	30,700	16,100	52	8.8
As	9.3	<2	NG	--
Ba	122	71.5	59	15
Be	NR	5.02	--	1.6
Cd	0.17	<0.04	NG	--
Co	6.8	6.4	94	4.7
Cr	34.4	20.6	60	4.8
Cu	16.5	<0.2	NG	--
Fe	11,100	6,520	59	6.4
Mn	28	19.5	70	5.8
Mo	NR	<0.09	--	--
Ni	19.4	12.3	63	6.9
Pb	12.4	<0.9	NG	--
Sb	0.58	<0.9	NG	--
Se	2.6	<0.9	NG	--
Ti	1,750	1,240	71	12
V	44	28.1	64	8.8
Zn	28	19.9	71	2.8

[a] Represents average of two determinations.

NG = Blank value is higher than sample.
NR = Not reported.

TABLE 4-23. ANALYSIS OF NBS COAL FLY ASH SRM 1633a BY SODIUM CARBONATE/SODIUM BORATE FUSION - QUANTITATION BY ICP WITH RAININ PUMP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	140,000	71,800	51	2
As	145	26.1	18	23
Ba	1,500	973	60	4
Be	12	45.8	382	6
Cd	1.0	<0.2	--	--
Co	46	38.0	83	9
Cr	196	156	80	8
Cu	118	121	103	126
Fe	94,000	48,100	51	5
Mn	190	103	54	--
Mo	29	<0.4	0	--
Ni	127	73.6	58	24
Pb	72.4	NG	--	--
Sb	7	5.5	79	84
Se	10.3	<4	--	--
Ti	8,000	6,200	77	3
V	300	197	66	3
Zn	220	195	89	8

[a] Represents average of three determinations.

NG = Blank value is greater than sample.

TABLE 4-24. ANALYSIS OF NBS COAL SRM 1632a BY HYDROFLUORIC ACID BOMB METHOD (ANAL. CHEM) - QUANTITATION BY ICP

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
Al	30,700	17,700	56	9
As	9.3	<3	--	--
Ba	12.2	66.4	54	11
Be	NR	2.5	--	13
Cd	0.17	<0.1	--	--
Co	6.8	4.5	67	17
Cr	34.4	31.4	91	38
Cu	16.5	16.6	101	102
Fe	11,100	6,200	56	10
Mn	28	14.9	53	15
Mo	NR	<0.2	--	--
Ni	19.4	21.9	113	74
Pb	12.4	<2	--	--
Sb	0.58	<2	--	--
Se	2.6	<2	--	--
Ti	1,750	507	28	30
V	44	22.2	50	14
Zn	28	40.1	143	76

[a] Represents mean of three determinations.

NR = Not reported.

TABLE 4-25. ANALYSIS OF NBS COAL SRM 1632a BY DILUTE NITRIC ACID SOLUBILIZATION OF LOW TEMPERATURE PLASMA ASHED COAL - QUANTITATION BY ICP

Element	Concentration (μg/g) Expected	$\bar{X}^a$	Mean % recovery	% RSD
Al	30,700	9,050	29	6
As	9.3	3.3	35	3
Ba	122	68.5	56	12
Be	NR	3.4	--	6
Cd	0.17	0.25	118	28
Co	6.8	6.1	90	2
Cr	34.4	16.4	48	4
Cu	16.5	13.8	84	1
Fe	11,100	9,360	84	8
Mn	28	23.2	83	<1
Mo	NR	<0.2	--	--
Ni	19.4	17.9	92	11
Pb	12.4	<2	--	--
Sb	0.58	2	--	--
Se	2.6	<2	--	--
Ti	1,750	75.7	4	<1
V	44	22.0	50	4
Zn	28	30.7	110	17

[a] Represents mean of two determinations.

NR = Not reported.

Average percent recoveries for analysis of NBS coal SRM 1632a by ICP, when prepared according to the methods previously described, are given in Table 4-26. No single preparative technique gave acceptable recoveries for all elements studied, although it appears that the use of two or three separate preparations could result in acceptable recoveries for most elements. No attempt was made to evaluate combinations of the procedures, e.g. taking a Parr-bombed sample and acid digesting it in HF/AR. The HF/AR digestion of low-temperature ashed coal gave the best overall recoveries for Al, Cr, Cu, Fe, Mn, Ti, V, and Zn and second best for Ni. However, this method and all the rest provided poor recoveries for the volatile elements Pb, Se, As, Sb, and trace elements Mo and Cd. Lead recoveries were reduced due to a known spectral interference with Al but it is not clear whether the sample preparation procedure also contributed to the low lead recoveries. The preparation methods resulting in the greatest percent recoveries are presented in Table 4-27.

Comparison of the HF/AR, Parr bomb, and LMB methods for preparation of muffle-furnace ashed real-world coal samples (Table 4-28) generally support the conclusion from the NBS coal study. Because there is no certified or reference concentration for any of these samples, the data must be examined for trends rather than absolute differences. Major elements were not determined for the Parr-bombed coals because this method gave very poor recoveries for these elements from the NBS coal.

Average percent recoveries for analysis of NBS fly ash SRM 1633a by ICP-AES, when prepared according to the methods previously described, are given in Table 4-29. As with the NBS coal, no single preparative technique gave acceptable recoveries for all elements studied (Table 4-30). Also, the methods demonstrating the best recoveries were somewhat different than for the coal. None of the techniques studied achieved acceptable recoveries for Be, Cd, Mo, Pb, or Se due to blank contamination, detection limits, and matrix effects.

Comparison of the HF/AR and LMB methods for preparation of real-world coal-fly-ash samples (Table 4-31) generally did not support the conclusions from the NBS fly ash study. Because there is no certified or reference concentration for any of these samples, the data must be examined for trends rather than absolute differences. Results for Al, Fe, Mn, and Ti

TABLE 4-26. COMPARISON OF AVERAGE PERCENT RECOVERIES FOR ANALYSIS OF NBS COAL SRM 1632a - QUANTITATION BY ICP

Element	LMB	Parr bomb		HF/aqua regia		Level 1 aqua regia	Sodium carbonate/ sodium bicarbonate		HF bomb	Nitric acid
	Muffle ashed	Benzoic acid	No benzoic acid	Muffle ashed	LTA ashed	LTA ashed	Muffle ashed	Not ashed	Not ashed	LTA ashed
Al	78	1	7	85	103	22	52	70	56	29
As	BD	52	20	NG	BD	BD	NG	NG	BD	35
Ba	63	<1	11	670	327	34	59	86	54	56
Be[a]	3.4	0.1	0.6	5.2	7.7	2.5	5.0	6.1	2.5	3.4
Cd	BD	112	24	88	BD	66	NG	BD	BD	118
Co	120	4	65	106	117	71	94	98	67	90
Cr	93	15	238	85	98	38	60	96	91	48
Cu	NG	4	238	90	101	37	NG	NG	101	84
Fe	88	2	14	85	97	67	59	76	56	84
Mn	88	3	109	61	101	61	70	80	53	83
Mo[a]	ND	1.4	0.7	NG	NG	BD	BD	BD	BD	BD
Ni	71	4	178	78	84	65	63	48	113	92
Pb	NG	11	BD	BD	BD	BD	NG	NG	BD	BD
Sb	BD	172	BD	525	BD	BD	NG	NG	BD	BD
Se	BD	54	BD	BD	BD	BD	NG	BD	BD	BD
Ti	93	<1	9	94	101	9	71	77	28	4
V	88	7	24	92	108	46	64	72	50	50
Zn	54	15	128	84	98	61	71	190	143	110

[a] Values determined by preparative techniques; concentration μg/g.

BD = Below detection.
NG = Blank higher than samples.
NR = Expected value not reported.

TABLE 4-27. PREPARATIVE METHODS DEMONSTRATING BEST AVERAGE PERCENT RECOVERIES OF EXPECTED METAL CONCENTRATIONS IN NBS COAL SRM 1632a - QUANTITATION BY ICP

Element	Lithium metaborate fusion	Parr oxygen bomb	HF/aqua regia digestion	Level 1 aqua regia	Sodium carbonate/ sodium borate fusion	HF bomb	Nitric acid LTA
Al			X				
As		X					
Ba					X		
Be							
Cd		X	X				
Co			X		X		
Cr	X		X		X		
Cu			X			X	
Fe	X		X				X
Mn	X	X	X				
Mo		X					
Ni			X			X	X
Pb		X					
Sb		X					
Se		X					
Ti	X		X				
Tl							
V	X		X				
Zn			X				

TABLE 4-28. COMPARISON OF MUFFLE FURANCE ASHED COAL SAMPLES PREPARED BY HYDROFLUORIC ACID/AQUA REGIA DIGESTION, PARR OXYGEN BOMB COMBUSTION AND LITHIUM METABORATE FUSION - QUANTITATION BY ICP

		Concentration (μg/g)								
	Sample ID	15256			15266			15268		
Element	Prep Method	HF-AR	Parr bomb	LMB fusion	HF-AR	Parr bomb	LMB fusion	HF-AR	Parr bomb	LMB fusion
Al		6,440	NA	6,610	5,170	NA	5,170	6,300	NA	6,630
As		8.5	6.2	19	2	2.3	<5	2	3.0	3.0
Ba		417	NA	720	244	NA	666	460	NA	803
Be		2.40	0.20	2.46	0.90	0.16	0.92	1.43	0.28	1.7
Cd		0.17	1.2	1.6	0.04	NG	NG	0.1	NG	NG
Co		1.4	NA	1.7	1.2	NA	1.5	1.6	NA	1.8
Cr		2.0	3.2	3.3	2.2	1.3	0.16	2.5	0.8	1.4
Cu		1.0	2.3	NG	1.7	0.3	NG	2.9	0.3	NG
Fe		11,500	NA	11,300	4,000	NA	4,190	6,350	NA	7,210
Mn		7.99	NA	7.0	24.8	NA	24.2	26.2	NA	27.8
Mo		<0.1	NA	NG	<0.1	NA	NG	<0.1	NA	NG
Ni		1.4	1.9	0.6	1.4	0.6	0.6	1.6	0.7	0.8
Pb		<1	<2	NG	0.8	<2	NG	<1	<2	NG
Sb		2	<2	NG	1	<2	NG	2	<2	NG
Se		NG	NG	NG	NG	NG	NG	NG	NG	NG
Ti		244	NA	225	168	NA	174	234	NA	254
V		2.8	NA	2.9	2.7	NA	3.0	2.9	NA	3.1
Zn		1.4	0.6	NG	0.68	NG	NG	3.0	1.7	NG

NA = Not analyzed.
NG = Blank value higher than samples.

TABLE 4-28 (continued)

Sample ID		Concentration (μg/g)								
		15256			15266			15268		
Element	Prep Method	HF-AR	Parr bomb	LMB fusion	HF-AR	Parr bomb	LMB fusion	HF-AR	Parr bomb	LMB fusion
Al		5,340	NA	6,900	5,480	NA	6,360	8,930	NA	7,510
As		5.4	4.2	<5.6	5.4	4.6	5.9	7	3.8	10
Ba		353	NA	668	209	NA	697	431	NA	820
Be		1.47	0.29	0.86	1.73	0.13	1.33	2.63	0.15	3.68
Cd		0.1	<0.1	NG	0.1	<0.1	NG	0.2	<0.1	NG
Co		0.97	NA	1.5	1.2	NA	2.2	1.3	NA	1.7
Cr		1.9	3.1	1.9	2.0	0.7	2.1	2.5	0.73	2.4
Cu		1.3	0.7	NG	2.5	0.4	18	17.0	0.7	40
Fe		6,570	NA	4,460	8,000	NA	6,910	12,400	NA	18,900
Mn		19.9	NA	31.1	22.5	NA	29.1	36.4	NA	26
Mo		<0.1	NA	NG	<0.1	NA	NG	<0.1	NA	NG
Ni		1.1	1.8	<0.9	20	0.4	124	1.8	NG	<1
Pb		<0.9	<2	NG	<0.9	<2	NG	<1	<2	NG
Sb		2	<2	<4	<1	<2	<4	<1	<2	<6
Se		NG	NG	NG	NG	NG	NG	NG	NG	NG
Ti		235	NA	238	233	NA	215	285	NA	260
V		3.0	NA	4.2	2.7	NA	NG	3.4	NA	NG
Zn		1.2	0.2	NG	1.4	0.2	NG	2.2	0.3	NG

NA = Not analyzed.
NG = Blank value higher than samples.

TABLE 4-28 (continued)

	Sample ID	Concentration (μg/g)					
		15272			15273		
Element	Prep method	HR-AR	Parr bomb	LMB fusion	HF-AR	Parr bomb	LMB fusion
Al		5,920	NA	5,280	6,560	NA	6,410
As		2	3.2	<7	4	5.3	7
Ba		607	NA	686	64.3	NA	731
Be		0.892	0.15	1.0	1.75	0.04	2.43
Cd		0.1	0.15	NG	0.1	0.1	NG
Co		1.3	NA	2.8	0.96	NA	1.7
Cr		1.3	4.5	22	2.2	12	2.4
Cu		1.4	1.0	23	1.9	1.5	1
Fe		3,760	NA	5,070	7,860	NA	11,200
Mn		26.1	NA	29.5	22.0	NA	299
Mo		<0.1	NA	NG	<0.1	NA	NG
Ni		1.1	3.0	544	7.2	2.2	3.4
Pb		<0.8	<2	NG	<1	<2	NG
Sb		0.8	<2	NG	2	<2	<4
Se		NG	NG	NG	NG	<2	NG
Ti		216	NA	171	274	NA	231
V		3.1	NA	3.2	2.9	NA	3.6
Zn		1.5	1.8	<0.2	0.99	1.0	NG

NA = Not analyzed.
NG = Blank value higher than samples.

TABLE 4-29. COMPARISON OF AVERAGE PERCENT RECOVERIES FOR ANALYSIS OF NBS COAL FLY ASH SRM 1633a - QUANTITATION BY ICP

Element	Lithium metaborate fusion	HF/aqua regia digestion	Level 1 aqua regia	Sodium carbonate/ sodium borate fusion
Al	96	63	1	51
As	BD	29	1	18
Ba	84	120	2	60
Be	303	480	5	382
Cd	BD	BD	BD	BD
Co	111	104	2	83
Cr	86	79	1	80
Cu	580	64	1	103
Fe	96	64	3	51
Mn	78	60	2	54
Mo	BD	BD	1	BD
Ni	77	76	2	58
Pb	NG	BD	BD	NG
Sb	BD	BD	BD	79
Se	BD	BD	BD	BD
Ti	106	84	1	77
V	93	74	2	56
Zn	111	80	2	89

BD = Below detection.

NG = Blank higher than sample.

TABLE 4-30. PREPARATIVE METHODS DEMONSTRATING BEST AVERAGE PERCENT RECOVERIES OF EXPECTED METAL CONCENTRATIONS IN NBS COAL FLY ASH SRM 1633a - QUANTITATION BY ICP-AES

Element	Lithium metaborate fusion	HF/aqua regia digestion	Level 1 aqua regia	Sodium carbonate/ sodium borate fusion
Al	X			
As		X		
Ba	X	X		
Be[a]				
Cd[a]				
Co		X		
Cr	X			
Cu				
Fe	X			
Mn	X			
Mo[a]				
Ni	X	X		
Pb[a]				
Sb				X
Se[a]				
Ti	X			
V	X			
Zn	X			X

[a] No results could be considered satisfactory.

TABLE 4-31. COMPARISON OF COAL FLY ASH SAMPLES PREPARED BY LITHIUM METABORATE FUSION AND HYDROFLUORIC ACID AQUA REGIA DIGESTION. QUANTITATION BY ICP-AES

		Concentration (μg/g)									
	Sample ID	15326		15327		15328		15329			
								LMB fusion		HF-AR	
Element	Prep method	LMB fusion	HF-AR	LMB fusion	HF-AR	LMB fusion	HF-AR	A	B	A	B
Al		38,200	24,300	46,400	31,800	29,500	12,700	52,900	55,400	38,300	34,100
As		<60	<15	<60	<15	<60	57	<60	100	<15	<15
Ba		3,210	NG	6,130	2,860	4,720	862	4,090	4,170	386	<0.5
Be		14	9.80	6.0	6.75	6.0	5.0	16	16	12.2	11.9
Cd		<2	0.9	<2	1	8	2	14	<2	1	1
Co		NG	5	NG	10	NG	7.0	<6	NG	7.2	5.6
Cr		24	16	40	26	42	32	16	52	19	17
Cu		618	18	NG	9.0	140	8.2	460	<4	9.3	8.5
Fe		64,900	51,200	35,400	26,800	30,300	19,300	73,100	74,700	57,500	55,500
Mn		1,260	1,130	1,330	1,120	1,140	951	878	872	778	792
Mo		<4	NG	<4	NG	<4	NG	<4	<4	NG	NG
Ni		<10	6.2	<10	11	<10	15	<10	<10	7.8	7.3
Pb		NG	<10	NG	<10	NG	<10	120	NG	<10	<10
Sb		NG	<10	<40	20	NG	<10	<40	NG	18	27
Se		<40	NH	<40	NG	<40	NG	<40	<40	NG	NG
Ti		1,260	1,040	2,030	1,590	1,980	1,530	1,720	1,700	1,430	1,320
V		10	16	<10	30	16	24	32	22	19	17
Zn		NG	13	NG	9.5	NG	20	NG	NG	11	15

NG = Blank higher than sample.

TABLE 4-31 (continued)

	Sample ID	Concentration (μg/g)						
		15323		15324			15325	
					HF-AR			
Element	Prep method	LMB fusion	HF-AR	LMB fusion	A	B	LMB fusion	HF-AR
Al		27,600	14,100	43,000	25,500	28,600	31,800	12,200
As		<60	<15	<60	<15	<15	<60	17
Ba		2,060	NG	5,550	2,070	1,910	4,940	1,520
Be		6.0	13.0	8.0	6.28	6.58	8.0	5.10
Cd		8	<0.5	<2	0.5	0.8	14	2
Co		NG	4	8	9.5	9.8	NG	9.3
Cr		56	16	50	27	30	84	35
Cu		NG	22	NG	14	14	NG	12
Fe		48,200	35,000	33,400	24,600	26,000	32,100	19,500
Mn		1,570	1,540	1,160	1,470	1,450	1,370	1,180
Mo		<4	NG	<4	NG	NG	<4	NG
Ni		<10	4	<10	11	6.6	10	17
Pb		NG	<10	NG	<10	<10	NG	<10
Sb		NG	<10	NG	<10	<10	NG	<10
Se		<40	NG	<40	NG	NG	<40	NG
Ti		908	859	1,920	1,840	1,800	2,190	1,840
V		<10	21	30	37	34	24	32
Zn		NG	14	NG	12	13	40	21

NG = Blank greater than sample.

TABLE 4-31 (continued)

	Sample ID	Concentration (µg/g)							
		15330		15331		15332		15333	
Element	Prep method	LMB fusion	HF-AR	LMB fusion	HF-AR	LMB fusion	HF-AR	LMB fusion	HF-AR
Al		54,600	49,500	31,800	15,900	40,100	33,700	52,300	8,520
As		<60	<15	<60	81	<60	NG	<60	NG
Ba		7,200	6,440	5,250	1,370	3,640	1,340	6,430	NG
Be		10	8.7	8	7.15	10	11.0	8	6.60
Cd		<2	0.7	26	2	<2	1	6	2
Co		10	16	NG	13	NG	7	10	9.3
Cr		<6	38	38	45	12	19	54	28
Cu		790	15	NG	17	NG	7.6	NG	19
Fe		36,000	30,800	30,700	25,500	51,500	47,600	30,400	22,000
Mn		1,040	1,070	1,110	1,260	1,330	1,310	1,150	1,280
Mo		<4	NG	<4	NG	<4	NG	<4	NG
Ni		<10	12	<10	23	<10	8.1	<10	13
Pb		NG	<10	NG	<10	NG	<10	NG	<10
Sb		NG	<10	NG	<10	<40	<10	144	20
Se		<40	NG	<40	NG	<40	<10	<40	<10
Ti		2,600	2,450	2,270	2,500	1,630	1,440	2,410	2,500
V		64	42	26	42	10	26	36	49
Zn		46	10	NG	37	NG	14	NG	9.1

NG = Blank higher than sample.

generally were similar for the real-world and NBS fly ash. Comparison of the results for the other elements is complicated by results that were reported as not detectable (As, Mo, Sb, Se, Cd) and/or were biased due to contamination introduced by the LMB flux (Co, Cu, Cd, Pb, Zn) or the HF/AR method blank (Se). The high Al levels also may have affected adversely the determination of Pb. Results for Cr were much different for the real-world as compared to the NBS fly ash with those determined using LMB nearly two times greater than from HF/AR.

Analyses of two older NBS SRMs for coal (1632) and fly ash (1633) were conducted by SSMS. Samples were prepared as described earlier; coal by Level 1 Parr oxygen bombing and fly ash by no procedure. These results are given in Tables 4-32 and 4-33 for 32 elements, although not the same 32 in each sample type. Mean percent recoveries based on the NBS expected values ranged from 9 to 183 percent with only Th, Pb, Sb, Rb, Cu, Mn, and K quantitated at 85 to 115 percent of their expected values for fly ash and La, Sr, As, Zn, Pb, Ca, and Cd for coal. As well as widely varying recoveries for each element, the precision of the determinations generally were poor, >40 percent RSD.

4.3.3.1.2 Other applications to coal and related materials--Vigler et al. (1980) described seven techniques for preparing samples for ICP-AES analysis in a petroleum laboratory. The preparation techniques are tailored to the sample matrix and the specific elements to be determined. This particular laboratory is interested in up to 24 elements and uses a simultaneous ICP-AES system. To limit losses of certain trace elements in procedures involving dry ashing, an "ash aid" is used. A magnesium or potassium organic sulfate is added to the sample before ashing light- to heavy-fuel distillates, asphalts, cokes, and coal. Dry ashing is used prior to determination of Al, As, Sb, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Pb, Mg, Mn, Mo, Na, Ni, Si, Sn, Ti, V, and Zn. The sample is heated in a crucible with ash aid and concentrated H_2SO_4 until white fumes are evolved. It is ignited and ashed at 650 °C in a muffle furnace. The resulting ash is dissolved in a dilute acid (HNO_3, HCl or H_2SO_4). Tartaric acid (0.04 percent) is added to solubilize Al, Si, and Ti. Solvent dilution is used to prepare lubricating oils for analysis for wear metals. The sample is diluted 1 g to 10 mL with either MIBK (methyl isobutyl ketone) or xylene to which Co has

TABLE 4-32. ANALYSIS OF NBS COAL SRM 1632 BY SSMS

Element	Concentration (μg/g)		Mean % recovery	% RSD
	Expected	$\bar{X}^a$		
U	1.4	0.14	10	55
Th	3.0	0.79	26	91
Ce	19.5	6.0	31	77
La	10.7	8.6	80	57
Ba	352	141	40	89
Cs	1.4	0.44	31	11
Sb	3.9	1.6	41	38
Sr	161	142	88	78
Rb	21	8.4	40	79
Br	19.3	1.0	5	36
Se	2.9	1.6	55	25
As	5.9	4.8	81	35
Zn	37	31	84	59
Ni	15	10.6	71	18
Co	6	1.8	30	35
Fe	8,700	1,620	19	77
Mn	40	20	50	78
Cr	20.2	37	183	122
V	35	8.4	24	12
Ti	800	285	36	37
Pb	30	24	80	74
Ca	4,300	4,600	107	108
K	2,800	500	18	28
Cl	890	17	2	35
Al	18,500	10,300	56	106
Mg	2,000	550	28	13
Na	414	140	34	80
Cu	18	22	122	9
Tl	0.59	0.16	27	50
Cd	0.19	0.20	105	25
Si	32,000	12,850	40	90
Be	1.5	0.32	21	94

[a] Represents mean of two determinations.

TABLE 4-33. ANALYSIS OF NBS SRM COAL FLY ASH (1633) BY SSMS

Element	Concentration (µg/g) Expected	Concentration (µg/g) $\bar{X}$[a]	Mean % recovery	% RSD
U	11.6	7.1	61	31
Th	24	22	92	54
Pb	70	64	89	10
Tl	4	0.94 - 6.1	--	--
Ce	146	110	61	75
La	82	99	121	56
Ba	2,700	4,000	118	42
Cs	8.6	5.2	60	60
I	2.9	0.67	23	19
Sb	6.9	7.3	106	42
Cd	1.45	0.36 - 1.9	--	--
Sr	1,400	2,000	143	42
Rb	112	100	89	37
Se	9.4	0.63 - 58	--	--
As	61	80	131	45
Zn	216	350	162	43
Cu	128	120	94	32
Ni	98	160	163	57
Co	38	50	132	50
Fe	62,000	79,000	127	30
Mn	493	540	110	39
Cr	131	69	53	58
V	214	280	131	57
Ti	7,400	8,700	118	37
Ca	4,300	7,300 - 230,000	--	--
K	2,800	3,100	111	100
Cl	890	320	36	72
Si	210,000	58,000	28	55
Al	127,000	12,000	9	78
Mg	18,000	9,700	54	97
Na	3,200	1,400	44	78
Be	(12)	8.1	68	74

[a] Represents mean of five determinations.

been added as an internal standard. A decrease in the Co emission signal indicates possible blocking of the nebulizer by small particles of wear metals. Solvent extraction is used to prepare uranium yellow cake for analysis of trace element impurities. The yellow cake is dissolved in HNO_3 and the U extracted with tributyl phosphate, leaving the trace elements in the acid. Residual extractant is removed by a separate extraction with CCl_4. A Teflon-lined acid digestion bomb is used to dissolve alloys, glass air filters, soils, fly ash, silicates, metals, ores, and Ti compounds. Silicates are dissolved by mixing 0.01 to 0.1 g of sample with 0.1 mL water, 3 mL concentrated HNO_3, 0.5 mL 48 percent HF and 5 mL HCl (1 + 3M). The bomb is sealed and heated in an oven at 120 °C for 4 h. After opening, 5 mL of 10 percent H_3BO_3 is added to convert excess HF to BF_3.

An oxygen bomb is used to combust samples such as oil, coal, and coke where recovery of the volatile elements As, Hg, Sb, and Pb are desired. A small Pt crucible holds the sample, which is ignited by an electric current in a pressurized oxygen atmosphere. During and after combustion, the bomb is kept in ice water to facilitate condensation of gases. The gases are absorbed by a small amount of weak acid or base added to the bomb.

Regardless of whether the bomb is equipped with a quartz liner, the entire bomb and all internal surfaces must be rinsed thoroughly to ensure quantitative recovery of elements. Acid dissolution in a Teflon beaker is used for samples that dissolve easily and for which recovery of volatile elements is not an objective. A 0.1 g sample is mixed with 0.1 mL of water in a Teflon beaker, 3 mL of concentrated HNO_3 is added and mixed, followed by 0.5 mL of 48 percent HF. The sample is heated until dissolved, and 5 mL of 10 percent H_3BO_3 is added to consume excess HF.

The sample is brought to 50 or 100 mL total volume with water at an acid concentration of 1 to 5 percent. Samples high in Cr are prepared as follows. A 0.1-g sample is mixed with 0.1 mL water, 3 mL HNO_3, and 0.5 mL HF sequentially in a Teflon beaker. Concentrated HCl (10 mL) is added carefully, the solution evaporated to 2-3 mL volume on a hot plate, cooled, and 3 mL concentrated H_2SO_4 added. The mixture is heated to fumes, cooled, and 5 mL 10-percent H_3BO_3 added to consume excess HF. If the sample is still not dissolved completely, more HF (0.5 mL) is added and the mixture heated again to H_2SO_4 fumes.

Acid-basic fusions are used to prepare coal, coke, shale oils, and silicates for Si analysis or to complete the dissolution of residues of asphalts, tars, or heavy bunker fuels treated by the use of ash aids. A 1:1 mixture Li_2CO_3 and H_3BO_3 is used to give a 5:1 Li/sample ratio. The fusion agents (1.5 g) are mixed with the ash (0.1 to 0.2 g) and fused in a Pt crucible at 750 °C in a muffle furnace for 15 to 30 min. The crucible is cooled to ambient temperature and 20 mL of 3N H_2SO_4/0.04 percent tartaric acid is added to dissolve the fusion melt by heating on a hot plate for 30 min to 1 h. The sample is diluted to 80 mL with water. This procedure results in a dilution factor of 10 for an 8 g sample that produced 0.1 to 0.2 g of ash.

Nadkarni (1980) compared high-temperature and low-temperature oxygen plasma ashing methods for coal. The ashed coal was then dissolved in a Parr bomb in a mixture of aqua regia and HF or fused in an automatic fusion device (the Claisse Fluxer) with $LiBO_2$. The samples dissolved in the acid digestion bomb required the addition of boric acid to dissolve insoluble fluorides. The fusion procedure produces a final solution (1L) that is too dilute for determination of the trace elements. Results for analysis of NBS SRM 1632 coal and NBS SRM 1633 fly ash for elements by these procedures using a simultaneous ICP-AES system are given in Tables 4-34, 4-35, and 4-36.

In a related study, Nadkarni (1981) determined volatile trace elements in coal shale oil and orchard leaves by ICP-AES after combustion and dissolution in a Parr oxygen bomb. The results are given in Table 4-37.

Shendrikar (1980), in an evaluation of methods for quantitation of trace elements emitted from utility boilers, analyzed coal and hopper ash by ICP-AES. Blind duplicates were supplied to the ICP-AES laboratory. Sample preparation involved low-temperature ashing followed by dissolution with HF in a Parr acid bomb. The results of the analyses of hopper ash (Table 4-38), pulverized feed coal (Table 4-39), and NBS SRM 1632a coal (Table 4-40) show considerable variation in terms of precision.

McQuaker et al. (1979) described the application of a comprehensive sample preparation procedure for waters, soils, biological tissues, and air particulates. The procedures are acid digestions involving HNO_3/$HClO_4$ and

TABLE 4-34. DISSOLUTION OF NBS-1633 FLY ASH IN PARR BOMB

Element[a]	Expected	Observed	% Bias
Al, %	12.5	11.6	-7
Ba	2,690	2,370	-12
Be	11.9	10.9	-8
Ca, %	4.60	4.8	-4
Co	39.3	26	-33
Cr	131	114	-13
Cu	128	136	+9
Fe, %	6.18	6.32	+2
K, %	1.68	1.51	-10
Mg, %	1.55	1.01	-35
Mn	493	482	-2
Mo	31	32	+3
Na, %	0.32	0.29	-9
Ni	98	128	+30
P	880	898	+2
Pb	70	77	+10
Si, %	20.5	20.4	0
Ti, %	0.72	0.75	+5
V	214	219	+2
Zn	210	210	0

[a] μg/g unless otherwise noted.

TABLE 4-35. COMPARISON OF HTA AND LTA ASH OF NBS COAL-1632 FOLLOWED BY ACID BOMB DISSOLUTION

Element, ppm	Expected	HTA	% Bias	LTA	% Bias
Al, %	1.78	1.86	+5	1.60	-10
As	5.9 ± 0.6	<6	--	<6	--
Ba	342	256	-25	183	-46
Be	1.45	1.77	+22	1.85	+28
Ca, %	0.41	0.45	+10	0.50	+22
Co	5.78	2.7	-53	4.9	-15
Cr	20.2 ± 0.5	18	-11	15	-26
Cu	18 ± 2	18	0	19	+6
Fe, %	0.87 ± 0.03	0.83	-5	0.80	-8
K, %	0.29	0.29	0	0.25	-14
Mg, %	0.16	0.14	-13	0.16	0
Mn	40 ± 3	45	-13	42	+5
Mo	3.82	3.3	-14	4.7	+23
Na	380	335	-12	409	-8
Ni	15 ± 1	19	+27	16	+7
Pb	30 ± 9	20	-33	15	-50
S, %	1.35	0.17	-87	0.90	-33
Si, %	3.38	3.17	-6	3.21	-5
Sn	10.1	8.0	-21	9.7	-4
Ti	960	942	-2	972	-1
V	35 ± 3	34	-3	33	-6
Zn	37 ± 4	36	-3	39	-5

TABLE 4-36. ANALYSIS OF NBS COAL AND FLY ASH STANDARDS BY CLAISSE FLUXER FUSION-ICPES

		Coal 1632				Fly Ash 1633		
Element, %	Expected	HTA ash	% Bias	LTA ash	% Bias	Expected	Observed	% Bias
Si	3.38	3.14	-7	3.19	6	20.5	22.4 ± 0.3	-9
Al	1.78	1.64	-8	1.66	-7	12.5	12.5 ± 0.3	0
Fe	0.87 ± 0.03	0.82	-6	0.88	+1	6.18	6.20 ± 0.04	0
Mg	0.16	0.12	-25	0.12	-25	1.55	1.29 ± 0.02	-17
Ca	0.41	0.40	-2	0.42	-2	4.60	4.62 ± 0.06	0
Na, ppm	380	370	-3	380	0	3,200	3,100 ± 200	-3
K	0.29	0.27	-7	0.27	-7	1.68	1.72 ± 0.09	+2
Ti	0.096	0.093	-3	0.096	0	0.72	0.71 ± 0.01	-1

TABLE 4-37. DETERMINATION OF VOLATILE ELEMENTS IN ORGANIC MATERIALS BY ICP-AES AFTER OXYGEN BOMB DISSOLUTION

Sample	Element	µg/g Expected	µg/g Observed	% Bias
Coal 1632a	As	9.3 ± 1	8.9 ± 1.2	-4
Coal 1632	As	5.9 ± 0.6	5.31	-10
Orchard leaves 1571	As	10 ± 2	8.9 ± 2.2	-12
Paraho Shale Oil	As	33 - 35	32	--
Green River Shale Oil	As	13.9	9.9	-29
Coal 1632	B	40	29	-28
Coal 1632a	B	53	22 ± 3	-58
Coal 1632	Pb	30 ± 9	19.1	-36
Coal 1632a	Pb	12.4 ± 0.6	6.9 ± 0.9	-44
Orchard leaves 1571	Pb	45 ± 3	31 ± 2	-31

TABLE 4-38. ANALYSIS OF HOPPER ASH BY ICP-AES

Element	Determinations, μg/g 1	 2
Al	91,144	126,094
Ba	148	397
Be	4.8	6.9
Cd	9.5	<17
Ca	1,555	4,482
Cr	67	141
Co	42	42
Cu	56	92
Fe	71,724	86,777
Pb	41	2.7
Mg	1,504	1,417
Mn	66	98
Mo	64	68
Ni	69	91
K	12,303	16,985
Ag	1.93	0.87
Na	1,559	1,871
Sr	131	163
Th	13.7	8.5
Sn	18.6	17.4
Ti	9,293	9,902
V	166	249
Zn	134	170

TABLE 4-39. ANALYSES OF PULVERIZED COAL BY ICP-AES

Element	Determinations, μg/g	
	1	2
Al	29,971	24,258
Ba	194	131
Be	1.38	2.4
Ca	2,091	1,048
Cd	<2	<2
Cr	25	22
Co	11.2	9.1
Cu	18.4	22
Fe	17,628	14,516
Pb	27	9.3
Mg	1,069	793
Mn	30	21
Mo	18	14
Ni	21	18.3
K	4,738	3,130
P	552	345
Ag	0.39	0.22
Na	508	365
Sr	145	98
Sn	6.87	13
Th	3.60	3.3
Ti	1,785	1,579
V	48	42
Zn	51	43
Zr	24.4	18.4

TABLE 4-40. ANALYSES OF NBS SRM 1632a COAL ICP-AES, µg/g

Element	Expected value	Mean[a]	% Bias
Al	30,700	27,556	-10
Cd	0.17	<6	--
Cr	34.4	26	-24
Co	6.8	10.5	+54
Cu	16.5	19.2	+16
Fe	11,100	11,662	+5
Pb	12.4	15.6	+26
Mn	28	28.8	+3
Ni	19.4	20	+3
Ti	1,750	1,625	-7
V	44	43	-2
Zn	28	39	+39

[a] Three blind replicates.

$HNO_3/HF/HClO_4$ treatments. The procedures result in a nearly constant $HClO_4$ content (3.5 ± 0.4 percent) in the final digest, requiring standards that match this level to reduce analytical error due to viscosity changes produced by variations in acid content, which affect the rate of sample uptake. All digestions are carried out in open 150-mL beakers at 250 °C on a hotplate in a perchloric acid fume cupboard. Reagent-grade acids were used: HNO_3 (65 percent), HF(42 percent), and $HClO_4$ (72 percent). In all cases, once the digests are taken to dense, white fumes of $HClO_4$, they are removed from the hotplate, cooled, diluted to 100 mL, and filtered using Whatman No. 42 paper. The $HClO_4$ fuming generally is accompanied by the digest going to a lighter color.

For water samples, 100 mL is evaporated to 5 mL in the presence of 5 mL HNO_3; an additional 5 mL HNO_3 is added and the sample taken to near dryness; 5.5 mL $HClO_4$ is added and the sample digested until $HClO_4$ fumes appear.

Homogenized soil samples (1.0 g, <100 mesh) are taken to near dryness in the presence of 10 mL HNO_3, 5.5 mL $HClO_4$ is added and the sample digested to $HClO_4$ fumes. A modified procedure used to solubilize silicon compounds requires 0.5 g sample, Teflon beakers, and taking the sample to dryness in the presence of HF after the NHO_3 step, and before the $HClO_4$ addition.

Previously homogenized plant or animal tissues are digested (1.0 g) in the presence of successive 15- and 10-mL aliquots of HNO_3 with the sample taken to near dryness after each addition. $HClO_4$ (5.5 mL) then is added and the sample digested to $HClO_4$ fumes. For determination of silicon compounds the sample is taken to dryness in the presence of HF after the HNO_3 digestion.

Air particulates collected using a high volume sampler are prepared by digesting two 46-mm diameter disks cut from the filter in 10-mL HNO_3 followed by 5.5-mL $HClO_4$ to $HClO_4$ fumes.

These sample preparation procedures were evaluated by digesting NBS SRMs and standard soil samples. Analyses were made using a simultaneous ICP-AES system. The results shown in Tables 4-41 and 4-42 indicate recoveries averaging 95 percent with precisions of 3- to 5-percent RSD.

TABLE 4-41. ANALYTICAL RESULTS (µg/g): BIOLOGICAL SAMPLES

Element	SRM 1571 Orchard Leaves				SRM 1577 Bovine Liver			
	NBS	AES[a]	% RSD	% Rec	NBS	AES[a]	% RSD	% Rec
As	10 ± 2	11		110				
Ba	44	42 ± 2	5	95				
Ca	20,900 ± 300	19,800 ± 500	3	95	123	127 ± 12	0	103
Cr	2.6	2						
Cu	12 ± 1	11 ± 1	9	92	193 ± 10	186 ± 2	1	96
Fe	300 ± 20	267 ± 6	2	89	270 ± 20	244 ± 2	1	90
Mg	6,200 ± 200	5,700 ± 60	1	92	605	573 ± 4	1	95
Mn	91 ± 4	86 ± 1	1	95	10.3 ± 1.0	10 ± 1	10	97
Mo					3.2	2		
P	2,100 ± 100	1,900 ± 40	2	90				
Pb	45 ± 3	42 ± 1	2	93				
Sr	37 ± 1	37 ± 1	3	100				
Zn	25 ± 3	26 ± 1	4	104	130 ± 10	131 ± 1	1	101
			mean 3%	96%			mean 4%	97%

[a] Results for seven replicate samples.

TABLE 4-42. ANALYTICAL RESULTS (μg/g): SOILS

Element	ELR-007				ELR-008			
	ELR[a]	AES[b]	% RSD	% Rec	ELR[a]	AES[b]	% RSD	% Rec
Al	63,700 ± 1,700	44,600 ± 2,900	6.5	70	66,500 ± 3,700	47,900 ± 3,400	7.1	72
Cd	20 ± 1	19 ± 1	5.3	95				
Cu	95 ± 6	91 ± 3	3.3	96	40 ± 1	36 ± 2	5.7	90
Fe	25,500 ± 100	23,300 ± 200	0.8	91	26,600 ± 300	23,500 ± 300	1.3	88
Mg	5,700 ± 2,170	5,990 ± 220	3.7	105	7,770 ± 2,080	7,160 ± 350	4.9	92
Mn	593 ± 13	449 ± 8	1.8	76	723 ± 15	615 ± 7	1.1	85
P	1,730 ± 250	1,570 ± 60	3.8	91	1,550 ± 60	1,630 ± 40	2.5	105
Pb	1,650 ± 60	1,520 ± 30	2.0	92	275 ± 96	295 ± 28	9.5	107
Zn	2,510 ± 70	2,500 ± 40	1.6	100	208 ± 10	208 ± 13	6.3	100
K	23,900 ± 800	21,500 ± 600	2.8	90	23,400 ± 1,300	22,900 ± 100	0.4	98
			mean 3.2%	91%			mean 4.3%	93%

---

[a] Uncertified reference values.

[b] Results of seven replicate samples.

Lynch et al. (1980) used the sample dissolution procedures of McQuaker et al. (1979) to prepare soil and airborne particulates collected near a lead/zinc smelter. Data were not reported for Si and B due to losses during sample preparation. HF could not be used to extract the glass Hi-Vol filters because it also extracted variable background levels of Na, K, Al, Fe, Ca, Mg, Ti, and P. Results are given in Table 4-43.

Hee et al. (1982) determined 21 elements in stack emissions from coal-fired power plants burning high- and low-sulfur coals. Emission samples of fly ash and other particulates were collected using a Method 5 Sample Train and the samples analyzed by ICP-AES using a simultaneous system. The samples were prepared by reacting with 10-mL 3:2-concentrated $HNO_3/HClO_4$ overnight in covered Teflon beakers. They were then refluxed at 90 °C until colorless, the HNO_3 evaporated, the temperature raised to 150 °C, and the $HClO_4$ evaporated. The residue then was reacted with concentrated HF (15 mL) at 120 °C until a clear solution was obtained. Then 2:1-concentrated HF/HNO_3 (15 mL) was added, the mixture heated for 2 h at 120 °C and 1 h at 150 °C, and evaporated to dryness at 120 °C. The residue was then brought to 10 mL with 8-percent HNO_3. Recoveries of Si were low due to HF volatilization losses. No data were presented. Elements determined were Al, B, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, Ti, and Zn.

Nadkarni and Botto (1984) reported on the determination of germanium in coal ashes by ICP-AES using a sequential spectrometer. The sample dissolution procedure adopted for coal and fly ash was chosen to minimize the loss of Ge due to its relatively high volatility. The use of HCl was avoided because volatile $GeCl_4$ boils at only 84 °C. Dry coal samples were ashed for 4 h in a muffle furnace in Pt crucibles at 450 °C. At this temperature no Ge losses were observed. Fly ash samples were not combusted further but were dried at 105 °C before analysis. Each ash (200 mg) was digested in 20 mL of 1:1:1 concentrated HF, HNO_3, H_2SO_4 and heated on a hotplate until mostly dissolved. Boric acid (2.5 g) was added to complex residual HF that could attack the ICP sample introduction system, and the mixture heated until all residual boric acid and fluorides were dissolved. Unburned carbon residue was removed by filtration through Whatman filter

TABLE 4-43. DETERMINATION OF ELEMENTS IN AIRBORNE PARTICULATES AND SOIL SAMPLES NEAR A LEAD/ZINC SMELTER BY ICP-AES

Element	Mean concentration, μg/g	
	Study air	Study soil
Al	4,580	8,990
Fe	7,020	14,400
Ca	6,540	4,830
K	2,520	2,290
Mg	2,020	3,440
Ti	294	472
Mn	502	284
Ba	202	180
Sr	79	58
Zn	18,100	2,630
Pb	28,100	1,590
As	10,100	49
Sb	2,140	49
Cd	1,330	17

paper. Filtrate and filter paper washings were combined and diluted to 100 mL. Ge standards had to be prepared in 3-percent H_2O_2 due to volatility losses observed when prepared in AR or AR/H_2SO_4. Results of analyses of coal and fly ash are given in Table 4-44.

4.3.3.2 Rocks and Soils--

Uchida et al. (1980) described a procedure for acid decomposition of silicate rocks. Powdered rock samples (0.5 g), HF (4 mL), and aqua regia (2 mL) are added to a Teflon vessel, which is sealed and left to stand for 16 h at room temperature. The contents then are transferred to a Teflon beaker and evaporated to near dryness at 95 °C on a hotplate; fumed with 2 mL of perchloric acid at 190 °C to remove tetrafluorosilicate and excess HF, and cooled. The residue is then dissolved with concentrated HCl (2 mL) and 30 mL water at 95 °C, and the solution diluted with water to 50 g. Elements were determined sequentially by ICP-AES. Mixed element standards were prepared in the same dissolution matrix. The spectral lines selected and the observed detection limit in the rock samples are given in Table 4-45. Accuracy and precisions for elements in standard rock samples are given in Table 4-46. Recoveries of Cr were low in some samples due to incomplete dissolution of Cr oxides.

Fogg and Seeley (1984) determined 13 elements in air particulates collected on filter paper using a Hi-vol sampler. The filters were analyzed by both instrumental neutron activation analysis (INAA) and an ICP-AES operated in the sequential mode. Quarter sections of the filters were ashed by low-temperature ashing in a Teflon vessel for 24 h, dissolved with 0.5 mL each of concentrated ultrapure HF and HNO_3 and brought to a final volume of 10 mL. ICP-AES analyses consisted of 3.3-s integrations using 2 mL of sample over a 10-min period for the 13 elements of interest. Analyses of replicate filter sections gave precisions of around 10-percent RSD. Good agreement between INAA and ICP-AES was obtained for all elements (Table 4-47) except Ca, Cr, Cu, and Mg. Of these, only the Cr results appear suspect due to ICP-AES problems. Accuracy was evaluated by analysis of HF/AR-ashed NBS SRM 1575 pine needles (Table 4-48). Although not a good model for air particulates, the results gave good agreement with the expected values.

TABLE 4-44. DETERMINATION OF GERMANIUM IN COAL AND FLY ASH BY ICP-AES

Sample	Expected value, µg/g	Reported value	% Bias
NBS SRM 1632 Coal	--	2.3 ± 0.1[a]	--
NBS SRM 1633 Fly Ash	23 ± 4[b]	26.8 ± 2.6[c]	--
NBS SRM 1633a Fly Ash	--	33.8 ± 3.4[d]	--
Pittsburgh Coal Fly Ash	--	37.6	--
Illinois Coal Fly Ash	--	23.3	--

[a] Two replicates.

[b] Gladney (1981).

[c] Five replicates.

[d] Six replicates.

TABLE 4-45. ANALYTICAL LINES AND DETECTION LIMITS

Element	Analytical line (nm)	Detection limit in silicate (ppm)	Element	Analytical line (nm)	Detection limit in silicate (ppm)
Ba	455.4	0.17	Ni	341.5	1.8
Co	345.3	2.6	Sc	361.4	0.068
Cr	267.7	0.59	Sr	407.7	0.013
Cu	327.4	0.91	V	310.2	0.67
Li	670.8	0.19	Zr	349.6	0.31

TABLE 4-46. ANALYTICAL RESULTS WITH ACCURACIES AND PRECISIONS FOR MINOR AND TRACE ELEMENTS IN STANDARD ROCK SAMPLES

Rock	Element	Expected (ppm)[a]	Observed (ppm)	Recovery (%)	RSD (%)
JG-1	Ba	466	463	100	2
	Co	6.4	-	-	-
	Cr	52.7	51.1	97	17
	Cu	3.9	-	-	-
	Li	94	86.4	92	3
	Ni	8.2	7.9	96	10
	Sc	6.5	5.4	83	3
	Sr	184.1	185	101	1
	V	24	24.9	104	3
	Zr	111	29.0	26	12
JB-1	Ba	490	486	99	1
	Co	39.1	45.6	117	3
	Cr	405	406	100	7
	Cu	55.7	56.1	101	2
	Li	11.4	10.7	94	3
	Ni	135	140	104	2
	Sc	26	26.3	101	1
	Sr	435.2	434	100	1
	V	211	215	102	3
	Zr	153	142	93	2
MRG-1	Ba	55	46.7	85	4
	Co	87	125	144	9
	Cr	420	308	73	1
	Cu	135	140	104	1
	Li	4	3.9	98	6
	Ni	200	196	98	1
	Sc	48	50.3	105	2
	Sr	260	271	104	1
	V	520	533	103	2
	Zr	100	110	110	3
AGV-1	Ba	1,208	1,200	99	2
	Co	14.1	13.8	98	8
	Cr	12.2	7.4	61	5
	Cu	59.7	61.2	103	2
	Li	12	12.4	103	1
	Ni	18.5	17.4	94	8
	Sc	13.4	13.0	98	4
	Sr	657	658	100	2
	V	125	124	99	2
	Zr	225	238	106	4

[a] Based on literature reported values.

TABLE 4-47. COMPARISON OF ICP-AES AND INAA FOR DETERMINATION OF TRACE ELEMENTS IN AIR PARTICLES[a]

Element	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	INAA	ICP	INAA	ICP	INAA	ICP	INAA	ICP	INAA	ICP
Na	349 ± 8.6	246 ± 14	135 ± 3.8	161 ± 15	233 ± 6.4	226 ± 3.1	276 ± 6.9	275 ± 8.0	374 ± 9.3	324 ± 7.2
Mg	58.5 ± 39	95.6 ± .41	61 ± 31	36.6 ± .22	46 ± 31	40.6 ± .43	127 ± 40	45.0 ± .33	119 ± 47	57 ± 1.0
Ca	73.5 ± 33	159 ± 1.7	73 ± 14	75.3 ± 1.1	62 ± 13	45 ± .26	56 ± 13	50.2 ± .32	34 ± 13	45 ± .06
Al	252 ± 3	272 ± 1.8	151 ± 3.1	141 ± 94	113 ± 2.6	94 ± .4	138 ± 2.9	134 ± .37	99 ± 2.1	100 ± 9.4
Cr	1.18 ± .05	4.14 ± .22	1.4 ± .06	.97 ± .20	1.5 ± .06	2.6 ± .18	.58 ± .04	1.79 ± .05	.17 ± .03	.71 ± .16
Ti	25.7 ± 8	20.0 ± .01	11.0 ± 2.9	11.8 ± .02	12.2 ± .06	8.2 ± .03	16 ± 2.3	8.95 ± .02	11 ± 3.1	7.0 ± .01
V	11.3 ± .53	11.9 ± .05	8.0 ± .2	8.2 ± .1	8.7 ± .19	8.6 ± 0.2	5.1 ± .12	5.2 ± .01	6.6 ± .16	6.5 ± .03
Mn	5.63 ± .16	5.96 ± .04	3.3 ± .13	2.8 ± .1	3.0 ± .13	2.6 ± .1	2.5 ± .06	2.0 ± .1	1.5 ± .05	1.2 ± .1
Fe	252 ± 9.1	229 ± .42	158 ± 6.9	126 ± .98	113 ± 5.7	102 ± .9	113 ± 5.2	101 ± .71	94 ± 4.7	65 ± .2
Co	0.20 ± .01	0.24 ± .03	.14 ± .006	.07 ± .01	.115 ± .008	.04 ± .04	.05 ± .01	.01 ± .03	.04 ± .005	<.02
Cu	8.00 ± 4.2	3.6 ± .03	3.4 ± 1.5	4.4 ± .02	<2	2.6 ± .01	2.5 ± 1.6	1.42 ± .01	.50 ± .55	1.10 ± .10
Zn	33.2 ± .54	29.6 ± .43	30.1 ± .6	22.4 ± .10	26 ± .64	19.9 ± .05	8.1 ± .29	5.04 ± .05	3.38 ± .21	2.05 ± .08
Ba	4.6 ± 1.3	3.69 ± .01	2.1 ± .88	1.9 ± .10	2.0 ± .90	1.7 ± .84	1.8 ± 1.0	1.6 ± .1	1.56 ± .93	1.03 ± 1

[a] Results expressed in micrograms per quarter filter. ICP-AES solution concentrations in mg/L may be obtained by dividing by 10.

TABLE 4-48. ANALYSIS OF NBS SRM 1575 (PINE NEEDLES) BY ICP-AES

Element	Wavelength (nm)	Expected value[a]	Measured value[a]
Al	308.22	545 ± 30	575 ± 1
Ca	315.89	0.41 ± 0.02%	0.400 ± .003%
Cd	214.44	<0.5	0.150 ± 0.02
Co	236.38	0.1	0.11 ± 0.02
Cr	205.55	2.6 ± 0.2	2.62 ± 0.2
Cu	324.75	3.0 ± 0.3	3.01 ± 0.5
Fe	238.20	200 ± 10	207 ± 0.8
Mn	257.61	675 ± 15	676 ± 0.7
Ni	231.60	3.5	3.7 ± 0.2
P	213.62	0.12 ± 0.02%	0.11 ± 0.005%
Pb	220.35	10.8 ± 0.5	10.8 ± 0.6
Sr	421.55	4.8 ± 0.2	4.75 ± 0.1

[a] Concentrations expressed as μg/g of dried material, or, where noted, in weight percent.

Motooka et al. (1979) used a selective extraction technique to prepare rock and soil samples for determination of Ag, Au, Bi, Cd, Cu, Pb, and Zn by ICP-AES. The 1-g samples are boiled with 1-g $KClO_3$ and 4-mL concentrated HCl. A mixture of 20-percent ascorbic acid 10-percent KI solution (8 mL) is added. Aliquot 336-MIBK (5 mL, 10 percent) is then added, the samples mixed, centrifuged, and the organic phase aspirated directly into the plasma. Aliquot 336 is tricaprylmethylammonium chloride, which selectively extracts trace elements but not major elements. Plasma instability is a problem when aspirating MIBK. This required a one hour warmup of time while aspirating MIBK followed by aspiration of the Aliquot-MIBK solution. In addition, molecular species formed by the MIBK reduced signals for some elements (Bi, Cd, Pb, and Zn). Detection limits in MIBK were also somewhat higher than in water (Table 4-49). Selected results for soil- and water-certified reference materials are given in Table 4-50.

Kuennen et al. (1982) used a simultaneous ICP-AES system to determine 14 elements in agricultural crops after their digestion in a pressurized Teflon bomb with HCl. The bomb method was compared with a total digestion procedure using HNO_3, $HClO_4$, and H_2SO_4 and was found to be a better method, because a higher sample throughput is possible as a result of reduced pretreatment time, and the need for fewer reagents and manipulations reduces the extent of sample contamination.

In the wet-digestion procedure, a 1-g sample is digested in 17.5 mL of a (3:2:2) nitric, perchloric, and sulfuric acid mixture to SO_3 fumes and diluted to 25 mL. The bomb method involves a 30-min pressure dissolution of a 1-g sample with 6-M HCl (25 mL) at 80 °C in a 60-mL polyethylene bottle. The sample bottles are agitated during the digestion. The cooled samples are filtered through a 10-µm Teflon filter and analyzed within 24 h. 70 to 95 percent of the sample dissolves in the bomb. Calibration standards consisted of aliquots of the sample matrix spiked with the elements of interest. Results of the analyses of peanuts, NBS wheat, and NBS spinach are given Tables 4-51, 4-52, and 4-53.

Uchida et al. (1979) described an acid dissolution procedure for preparation of silicate rocks for the determination of major elements (Si, Fe, Mn, Al, Mg, K, Ti, and Na). A powdered sample (50 mg) is digested at

TABLE 4-49. COMPARISON OF ICP-AES DETECTION LIMITS FOR ELEMENTS IN MIBK AND WATER

		Detection limit, μg/L[a]	
Element	λ, nm	MIBK	Water
Ag (I)	328.0	3	6
Au (I)	242.8	8	11
Bi (I)	306.7	120	200
Cd (II)	226.5	15	3
Cu (I)	324.7	2	2
Pb (II)	220.3	340	4.6
Zn (II)	202.5	100	4

[a] Concentration of element that will give a net signal intensity 2 times the standard deviation of the background.

TABLE 4-50. SELECTED RESULTS USING EXTRACTION COMPLEXATION SAMPLE PREPARATION PROCEDURE--MEANS OF 5 REPLICATE PLASMA ANALYSES (NOT DIFFERENT ALIQUOTS UNIQUELY PREPARED)

µg/g

Element	GXR-2 soil	GXR-5 (B horizon soil)	GXR-6 (B horizon soil)
Ag	17.7 (3)	0.77 (3)	0.35 (9)
Au	ND	ND	0.12 (8)
Bi	ND	ND	ND
Cd	4.7 (6)	0.22 (18)	0.18 (28)
Cu	71.0 (3)	323.0 (6)	54.0 (2)
Pb	651 (6)	15.0 (13)	96.0 (7)
Zn	670 (6)	37.0 (8)	104.0 (12)

( ) = % RSD

ND = Not detectable.

TABLE 4-51. SPIKED RECOVERIES, PEANUTS[a]

Element	Spiked amt, μg/g	Mean % recovery
Be	10	100.0 ± 1.8
Ca	1,000	101.0 ± 2.1
Cd	10	99.2 ± 1.6
Cr	10	98.4 ± 1.7
Cu	10	101.0 ± 2.8
Fe	10	98.5 ± 7.1
K	5,000	103.0 ± 3.1
Mg	1,000	101.0 ± 4.4
Mn	10	99.7 ± 3.9
Mo	10	95.6 ± 3.3
Ni	10	99.5 ± 1.8
P	2,000	103.0 ± 3.4
Pb	10	99.1 ± 3.4
Zn	10	102.0 ± 7.4

[a] 21 spiked determinations.

TABLE 4-52. NBS WHEAT[a] (1567)

		Results, µg/g		
			HCl dissolution	
Elements	Certified values, µg/g mean σ[b]	Wet digestion calibration curve mean σ[b]	Std addition mean σ[b]	Real sample matrix calibration curve mean σ[b]
Be	c	<0.03	<0.03	<0.03
Ca	190 ± 10	195 ± 2	195 ± 3	196 ± 2
Cd	0.032 ± 0.007	0.03 ± 0.02	0.03 ± 0.02	0.03 ± 0.02
Cr	c	<0.250	<0.250	<0.250
Cu	2.00 ± 0.30	2.06 ± 0.04	2.06 ± 0.03	2.00 ± 0.01
Fe	18.3 ± 1.0	18.4 ± 1.0	18.7 ± 2.1	17.7 ± 0.7
K	1,360 ± 40	1,330 ± 20	1,320 ± 10	1,320 ± 10
Mg	c	398 ± 10	419 ± 4	406 ± 3
Mn	8.50 ± 0.5	8.58 ± 0.16	8.67 ± 0.12	8.55 ± 0.15
Mo	(0.4)	0.40 ± 0.04	0.42 ± 0.04	0.38 ± 0.03
Ni	(0.18)	<0.500	<0.500	<0.500
P	c	1,370 ± 10	1,350 ± 20	1,400 ± 10
Pb	c	<3.8	<3.8	<3.8
Zn	10.6 ± 1.0	11.0 ± 0.2	11.1 ± 0.4	10.9 ± 0.1

[a] Six analyses, 1-g samples.

[b] Standard deviation.

[c] No certified values.

TABLE 4-53. NBS SPINACH[a] (1570)

Elements	NBS values, µg/g mean σ[b]	Results, µg/g		
			HCl dissolution	
		Wet digestion calibration curve mean σ[b]	Std addition mean σ[b]	Real sample matrix calibration curve mean σ[b]
Be	c	<0.03	<0.03	<0.03
Ca	13,500 ± 300	12,900 ± 300	13,500 ± 250	13,800 ± 140
Cd	(1.5)	1.45 ± 0.07	1.42 ± 0.03	1.41 ± 0.03
Cr	4.6 ± 0.3	4.3 ± 0.7	3.5 ± 0.3	3.54 ± 0.3
Cu	12 ± 2	11.8 ± 0.3	12.0 ± 0.3	12.2 ± 0.1
Fe	550 ± 30	530 ± 11	470 ± 50	540 ± 10
K	35,600 ± 300	35,200 ± 1,000	35,700 ± 400	35,300 ± 320
Mg	c	8,600 ± 230	8,790 ± 150	8,580 ± 65
Mn	165 ± 6	165 ± 3	172 ± 5	171 ± 1
Mo	c	<0.300	<0.300	<0.300
Ni	(6)	5.51 ± 0.32	6.17 ± 0.72	6.03 ± 0.52
P	5,500 ± 200	5,300 ± 70	5,240 ± 70	5,350 ± 45
Pb	1.2 ± 0.2	<3.8	<3.8	<3.8
Zn	50 ± 2	49.8 ± 1.3	50.6 ± 1.3	51.2 ± 0.6

[a] 14 analyses, 0.500-g samples.

[b] Standard deviation.

[c] No certified values.

room temperature for 4 h in a sealed Teflon vessel to which HCl (1 mL) and HF (0.5 mL) have been added. Boric acid (6 mL, 4 percent w/v) is added to the digested sample and the contents diluted with water to 100 g. The accuracy of the procedure was evaluated by the analysis of standard silicate rocks (Tables 4-54 and 4-55).

Burman et al. (1978) described a metaborate fusion method that was used to prepare silicate rocks for ICP-AES analysis. The typical ratio of fusing agent to sample is 7-10:1. This tends to result in clogging of the nebulizer with salts from the fusion, limiting the levels of fused sample that can be tolerated and also the analytical range. Drift in the emission readings is also common with fused samples. Nebulizer clogging can be reduced by appropriate sample dilution, but this reduces the sensitivity of the method. To minimize these problems, a much lower ratio (1:1) of $LiBO_2$ to sample was used. Sample (50 mg) and $LiBO_2$ (50 mg) were fused in a graphite crucible at 1,000 °C for 30 min. The borate beads formed from the fusion were dissolved in 8-percent (v/v) HNO_3 over 4 h and the solution diluted to a final volume of 100 mL. Levels of Si, Al, Ti, Ca, Mg, Na, Fe, Mn, Cr, Ba, Zr, and Cu were determined in silicate rocks prepared by this procedure using a sequential ICP-AES.

Walsh (1980) described a fusion method for determining major elements in silicate rocks. The conventional complete analysis of such samples involves the determination of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, MnO, and P_2O_5 at the percent level. These oxides are determined as the element and the results are reported on an oxide basis. For the fusion method, rock powder (0.5 g) and $LiBO_2$ (2.0 g) are mixed and fused in a Pt crucible over a Meker burner for 30 min. The crucible is cooled to room temperature and immersed in a 250-mL polyethylene beaker containing 200 mL cold 5-percent HNO_3. A magnetic stirrer is placed inside the crucible and the mixture stirred for 1 to 2 h or until the fusion bead is dissolved. The solution is then brought to 250 mL volume and analyzed by ICP-AES. Calibration curves are generated using USGS rock standards prepared in the same manner as the samples. Results for analyses of several standard rock samples are compared with expected values in Table 4-56.

TABLE 4-54. ACCURACY AND PRECISION IN THE ANALYSIS OF BASALT JB-1

Component	Certified value %	Value found %	Recovery %	RSD[a] %
SiO_2	52.09	52.3	100.4	0.88
Al_2O_3	14.53	14.8	101.9	0.67
Fe_2O_3	9.04	8.91	98.6	0.97
TiO_2	1.34	1.32	98.5	1.10
MnO	0.16	0.16	100	1.40
CaO	9.21	9.20	99.9	0.85
MgO	7.70	7.80	101.3	0.91
Na_2O	2.79	2.76	98.9	1.90
K_2O	1.42	1.40	98.6	1.85

[a] For six analyses.

TABLE 4-55. ANALYTICAL RESULTS (%) FOR STANDARD SILICATE SAMPLES (DUPLICATE ANALYSES)

Component		JG-1 Granodiorite	AGV-1 Andesite	MRG-1 Gabbro	R 701 Feldspar	NBS No. 91 Opal glass
SiO_2	found	72.6	60.1	38.5	68.1	67.0
	certified	72.24	59.00	39.24	67.98	67.53
Al_2O_3	found	14.6	17.1	8.22	17.6	5.80
	certified	14.21	17.25	8.56	17.31	6.01
Fe_2O_3	found	2.13	6.76	18.1	0.09	0.08
	certified	2.21	6.76	17.80	0.09	0.08
TiO_2	found	0.28	1.06	3.75	0.01	0.03
	certified	0.26	1.04	3.75	0.01	0.019
MnO	found	0.066	0.099	0.18	--	--
	certified	0.06	0.097	0.17	--	--
CaO	found	2.20	5.00	14.9	--	10.4
	certified	2.18	4.90	14.72	--	10.48
MgO	found	0.74	1.51	13.5	--	--
	certified	0.73	1.53	13.51	--	--
Na_2O	found	3.59	4.18	0.72	3.34	8.69
	certified	3.39	4.26	0.71	3.35	8.48
K_2O	found	4.05	2.96	0.19	10.8	3.37
	certified	3.96	2.89	0.18	10.41	3.25

TABLE 4-56. MAJOR OXIDE RESULTS FOR NIM INTERNATIONAL STANDARD ROCKS DETERMINED BY ICP-AES

Oxide %	NIM-G			NIM-N		
	Observed	Expected	% Bias	Observed	Expected	% Bias
SiO_2	75.2	75.7	-1	53.6	52.64	+2
Al_2O_3	11.68	12.08	-3	16.37	16.50	-1
Fe_2O_3	1.89	2.04	-1	8.76	9.10	-4
MgO	0.06	0.06	0	7.37	7.50	-2
CaO	0.76	0.78	-3	11.46	11.50	0
Na_2O	3.08	3.36	-8	2.38	2.46	-3
K_2O	4.94	4.99	-1	0.47	0.25	+88
TiO_2	0.09	0.09	0	0.19	0.20	-5
P_2O_5	0.00	0.01	-100	0.03	0.03	0
MnO	0.01	0.02	-50	0.17	0.18	-6

Floyd et al. (1980) used a NaOH-fusion HCl-dissolution procedure to prepare coal, fly ash, sediment, and rock samples for analysis by a sequential ICP-AES. All samples were diluted 500-fold before analysis. A single set of spectral lines was used (Table 4-57) and all elements were determined in sequence. Considerable effort was expended in advance to determine the ideal lines to use. Profiles of emission intensity vs wavelength were taken for the four strongest emission lines for each element. Also, spectra of single element solutions of known interferents likely to be present in these type samples (Al, Ca, Fe, Mg, Cr, Cu, Mn, Ni, Ti, and V) were also profiled over the same wavelength region. Detection limits given in Table 4-57 correspond to the concentration of an element required to give a net signal equal to three times the standard deviation of the background. The average and standard deviation of the background were obtained at a preselected wavelength adjacent to each element's emission line while a multielement reference solution was analyzed. The average and standard deviations of the gross signal were obtained at the element wavelength. Precision and accuracy of the method were evaluated for the SRMs given in Tables 4-58 through 4-61. Only values greater than five times the detection limit were reported.

Maazoori (1980) determined Mo, Co, and B in soil extracts by ICP-AES. A separate extraction procedure was required for each element. Ca and Mg interfered with the determination of Mo by enhancing the signal. Mo had to be quantitated by standard additions. Detection limits observed were Mo (0.01 ppm), Co (0.05 ppm), and B (0.05 ppm). Precision as percent RSD was 0.9 percent at levels 100 times the detection limit.

Soltanpour et al. (1979) determined P, K, Zn, Fe, Ca, and Mn in NH_4HCO_3-DPTA extracts of soil. The extracts had to be treated with 1:4 HNO_3 to prevent clogging of the nebulizer with precipitated carbonates and bicarbonates. Precision as RSD for triplicate analyses was 3 percent over the concentration range 2 to 400 ppm.

Lechler et al. (1980) analyzed 12 reference soils from the southeastern United States for major and minor elements using a simultaneous ICP-AES system. Separate sample preparation procedures were required for major and minor elements. For major elements, the soil samples were first ashed at

TABLE 4-57. DETECTION LIMITS OF GEOLOGICAL MATRICES

Element	Wavelength nm	Detection limits, μg/g	Element	Wavelength, nm	Detection limits, μg/g
Al	308.2	1	Nd	430.4	1.5
As	197.2	5	Ni	231.6	1
Ba	455.4	0.25	Pb	220.4	10
Be	313.0	0.03	Pd	340.5	0.5
Bi	223.1	2.5	Pr	390.8	0.1
Ca	315.9	0.05	Re	221.4	2
Cd	214.4	0.5	Rh	233.5	5
Ce	413.8	2	Ru	240.3	4
Cr	267.7	0.5	Sb	217.6	15
Co	228.6	1	Sc	361.4	0.05
Cu	324.8	0.2	Se	196.0	35
Dy	353.2	0.5	Sm	359.3	6
Er	337.3	0.5	Sn	235.5	5
Eu	420.5	0.25	Sr	407.8	0.01
Fe	238.2	0.25	Ta	226.2	8
Ga	294.4	3	Tb	350.9	0.5
Gd	342.3	2	Te	214.3	2
Ge	265.1	10	Th	283.7	5
Hf	277.3	1	Ti	334.9	0.2
Ho	389.1	0.5	Tl	351.9	4
In	230.6	10	Tm	346.2	2
Ir	224.3	0.3	U	386.0	6
La	394.9	1	V	310.2	0.1
Lu	261.5	0.1	W	207.9	5
Mg	279.6	0.02	Y	371.0	0.04
Mn	257.6	0.05	Yb	328.9	0.05
Mo	202.0	3	Zn	213.9	0.1
Nb	316.3	0.5	Zr	343.8	0.5

TABLE 4-58. ANALYTICAL RESULTS OF NBS SRM No. 1633 COAL FLY ASH[a]

Element	Al[b]	NBS	Ondov	Fisher
Al	12.8%		12.7%	12.7%
Ca	4.5%		4.7%	4.3%
Fe	6.0%		6.2%	6.4%
Mg	1.8%		1.8%	1.2%
Ti	7,330		7,400	6,800
As	56	61	58	
Ba	2,800		2,700	2,210
Be	11	12		12
Ce	140		146	
Co	41	38	42	42
Cr	123	131	127	128
Cu	120	128		121
Eu	2		25	
Ga	72		77	
La	78		82	
Mn	510	493	496	485
Ni	94	98	98	99
Pb	81	70	75	70
Pr	24			
Sc	20		27	
Sr	1,620	1,380	1,700	1,340
V	233	214	235	
Y	65		62	
Yb	7		7	
Zn	212	210	216	221
Zr	288		301	

[a] μg/g unless % indicated.

[b] Ames Laboratory result. Average of 10 determinations.

TABLE 4-59. ANALYTICAL RESULTS OF USGS COAL SAMPLES[a]

	PAS 44		PAS 47		PAS 48	
	AL[b]	USGS[c]	AL	USGS	AL	USGS
Zn	141	140	185	200	85	90
Co	40	36	80	89	30	32
Ni	85	96	179	170	88	84
Mn	105	103	249	235	300	297
Cr	104	99	200	236	131	120
Ga	68	52	43	51	38	46
V	136	152	189	195	198	195
Be	28	27	14	15	17	17
Cu	61	54	60	56	61	52
Yb	9	7	5.8	4	6	4
La		<5	73	75	81	83
Sc	30	27	41	39	18	25
Y	85	89	78	82	78	71
Eu	2.7		2.0		2.1	
Ba	200	193	340	337	405	381
Pr	4.6		17		14	
Sr	423	498	401	406	1,025	985

[a] Samples collected at a Pittsburgh coal bed, Washington County, PA. Literature values are not certified. Concentrations are in μg/g.

[b] Ames Laboratory result. Average of 5 determinations.

TABLE 4-60. ANALYTICAL RESULTS OF NBS SRMS[a]

	NBS SRM No. 1645 (river sediment)		NBS SRM No. 1648 (urban particulate matter)	
Element	AL[b]	NBS	AL[b]	NBS
Al	3.9%	4.0%	3.3%	3.3%
Ca	4.2%	4.0%		
Fe	11.5%	11.3%	4.1%	3.9%
Mg	4.1%	4.0%	0.9%	0.8%
Ti			0.4%	0.4%
As	71	66	112	115
Ba	400		774	737
Be	1		3	
Cd	10	10	73	75
Ce			61	55
Co	11	8	28	18
Cr	3.02%	2.96%	398	403
Cu	119	109	598	609
Eu	0.7		1	0.8
Ga	38		72	
La	15	9	35	42
Mn	750	785	851	860
Ni	45	46	85	82
Pb	725	714	0.7%	0.7%
Pr	14		8	
Se	5	2	4	7
Sr	1,200		450	
V	25	24	106	130
Y	7		5	
Yb	0.6		2	
Zn	1,587	1,720	4,700	4,760

[a] μg/g unless % indicated.

[b] Results are the average of 5 determinations.

TABLE 4-61. ANALYTICAL RESULTS OF USGS STANDARD ROCK SAMPLES[a]

	BCR-1		DTS-1		GSP-1		PCC-1	
	AL[b]	USGS[c]	AL	USGS	AL	USGS	AL	USGS
Al	16.8%	13.6%	0.2%	0.2%	14.5%	15.2%	1.0%	0.8%
Ca	6.9%	6.9%	0.1%	0.1%	2.2%	2.0%	0.5%	0.5%
Fe	13.7%	13.4%	8.4%	8.6%	4.3%	4.3%	9.0%	8.4%
Mg	3.7%	3.5%	d	49.8%	1.1%	1.0%	d	42.0%
Ti	2.1%	2.2%	120	130	0.7%	0.7%	137	150
Ba	661	675	2.5	2.4	1,290	1,300	1.4	1.2
Be	2.9	1.7			1.8	1.5		
Ce	50	54			401	394		
Co	41	38	141	133	12	7	130	112
Cr	19	18	2,110	3,600	16	12	1,585	2,730
Cu	18	18	6.6	7	40	33	9	11
Dy	7	6			6.8	5.4		
Er	4	4						
Eu	2.5	1.9			2.0	2.4		
Ga	19.6	20			27	22		
Gd					19	15		
Hf					17	16		
Ir							7	5
La	24	26			202	191		
Lu	0.6	0.5						
Mn	1,455	1,406	960	969	317	331	905	959
Nb	13.4	13.5			36	29		
Nd	32	29			175	188		
Ni	30	16	2,390	2,270	17	13	2,681	2,339
Pr	5	7			45	50		
Sc	29	33	3.5	3.6	7.4	7.1	6.6	6.9
Sr	338	330	0.3	0.4	241	233		
Th	7.5	6.0			92	104		
V	375	399	10.2	10.3	60	53	38	30
Y	36	37			28	30		
Yb	3.6	3.4			1.6	1.8		
Zn	158	120	51	45	112	98	44	36
Zr	209	190	2.5	3	523	500	7	7

[a] µg/g unless % indicated.

[b] Ames Laboratory result. Average of 10 determinations.

[c] Floyd et al. (1980).

[d] Concentrations out of calibration range.

1050° C in a muffle furnace and 100 mg of the ash dissolved in 2-mL AR and 3-mL HF in a sealed Teflon bomb at 140 °C for 1 h. The minor element sample preparation involved acid digestion in concentrated HNO_3 followed by more HNO_3, $HClO_4$, and HF and finally HCl. Major elements determined were Si, Al, Fe, Ca, Mg, Na, K, Mn, Ti, and P. Minor elements determined were Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sr, Th, V, Zn, and Y.

Moselhy and Vijan (1981) analyzed sewage sludge samples digested in aqua regia using a simultaneous ICP-AES system. Results of analyses of two quality control samples are shown in Table 4-62.

Clevenger et al. (1983) analyzed municipal wastewater treatment sludge for elements by ICP-AES. A 1-g sample was digested in 20-mL subboiling concentrated HNO_3 and $HClO_4$ to $HClO_4$ fumes. The digested sample was brought to 100 mL. Pb could not be determined due to an Al interference. Accuracy and precision data are given in Table 4-63.

Blakemore and Billedeau (1981) determined Ca, Cu, and Zn in animal feed by ICP-AES. Samples (1 g) were low-temperature ashed for 1 h, the residue dissolved in 10 mL of 1 $NHNO_3$, and brought to 25-mL total volume. Detection limits based on a signal equal to twice the background emission were Ca (1 ppm), Cu (0.5 ppm), and Zn (0.5 ppm). Results of analyses of spiked feed samples are given in Table 4-64.

Aten et al. (1983) determined Mg, Fe, and Zn in fertilizers using a sequential ICP-AES. The samples were dissolved in HCl, boiled to dryness, picked up in water, and filtered. Typical results, shown in Table 4-65, are compared with flame atomic absorption analyses of the same samples.

Jones (1982) determined nine elements in 34 Magruder fertilizer standards and the P content in ammonium citrate extracts of 17 standards using a simultaneous ICP-AES. Fertilizer samples were prepared by digesting 1 g in 10-mL (38 percent) HCl and 5-mL (69 percent) HNO_3 to fumes of each. Samples were brought to 1 L with distilled water prior to analysis. Typical results are given in Table 4-66 and the range of recoveries reported for all samples are given in Table 4-67.

The sample preparation problems that have been addressed here are not necessarily unique to the ICP/DCP sample introduction system. Indeed, the same procedures and problems are common to all methods that require the

TABLE 4-62. REVIEW OF INORGANIC QUALITY CONTROL

Element	Average % deviation of duplicates[a]	Average % recovery of spikes[a]
B	8.1	89
Be	8.4	100
Ca	1.8	b
Cd	1.7	97
Cr	5.4	89
Cu	2.4	98
Fe	8.5	b
K	12	b
Mg	4.2	b
Mn	1.6	95
Na	10	b
Ni	4.0	95
P	3.7	b
Zn	1.3	97

[a] 10% of the sludge samples were run in duplicate and 10% in spikes. This represents about 27 of each. Results are based on an average of these samples.

[b] Not spiked because concentrations too high.

TABLE 4-63. TYPICAL RESULTS FOR SELECTED SAMPLES MEASURED BY ICP (ALL CONCENTRATIONS ARE IN mg/L)

	Quality control A			Quality control B		
Element	Expected	Found	S.d.	Expected	Found	S.d.
Fe	2.0	2.07	0.17	4.0	3.88	0.31
Al	2.0	1.87	0.19	4.0	3.49	0.35
Ca	25.0	24.8	1.89	50.0	48.3	3.59
Zn	0.4	0.42	0.08	0.8	0.78	0.09
Cd	0.4	0.40	0.03	0.8	0.76	0.06
Co	0.5	0.47	0.04	1.0	0.89	0.08
Mg	10.0	9.77	0.85	20.0	18.7	1.52
Mn	0.4	0.39	0.03	0.8	0.74	0.06
Cr	0.5	0.48	0.04	1.0	0.91	0.07
Cu	0.4	0.41	0.07	0.8	0.74	0.10
Ni	1.0	1.01	0.08	2.0	1.91	0.15
Pb	0.5	0.51	0.06	1.0	0.98	0.08
Mo	0.2	0.21	0.02	0.4	0.40	0.03
Sr	0.2	0.20	0.02	0.4	0.40	0.05
Ti	--	--	--	--	--	--
V	0.2	0.18	0.02	0.4	0.36	0.03

TABLE 4-64. ANALYSIS OF ANIMAL FEED BY ICP-AES

Element	μg/g added	Recovered[a] ppm	Recovered[a] % recovery
Calcium	0	11,700 ± 170	--
	500	12,100 ± 170	85.0 ± 2.9
	1,000	12,500 ± 210	86.6 ± 3.2
	1,500	13,300 ± 240	107.0 ± 3.5
Copper	0	11.8 ± 0.1	--
	2	13.7 ± 0.15	95.0 ± 2.1
	4	15.5 ± 0.4	92.5 ± 4.2
	6	17.3 ± 0.3	91.7 ± 3.4
Zinc	0	111 ± 1.4	--
	10	120 ± 1.0	90.0 ± 1.7
	20	132 ± 2.9	105.0 ± 3.6
	30	140 ± 1.7	96.7 ± 2.8

[a] Mean and standard deviation (n-1) from triplicate assays.

TABLE 4-65. DETERMINATION OF Mg, Fe, AND Zn IN FERTILIZER[a]

Mg		Fe		Zn	
ICP	AA	ICP	AA	ICP	AA
0.287	0.312	0.182	0.185	0.334	0.330
2.09	2.11	0.810	0.801	0.529	0.519
7.59	7.24	2.87	2.73	0.953	0.918

[a] Wt. percent.

TABLE 4-66. DETERMINATION OF ELEMENTS IN FERTILIZER STANDARDS, wt %

Element	Spectral Line, nm	Sample 6908			Sample 6901		
		Expected	Observed	% Bias	Expected	Observed	% Bias
B	249.7	0.031	0.032	+3	--	--	--
Ca	422.6	4.09	3.93	-2	12.25	12.28	0
Cu	327.4	0.002	0.002	0	0.037	0.036	-3
Fe	259.9	0.350	0.470	+34	0.418	0.370	+11
Mg	279.5	1.08	1.03	-5	1.08	1.38	+28
Mn	257.6	0.117	0.102	-13	0.089	0.087	+2
P	214.9 × 2	11.82	11.89	+1	10.85	10.89	0
K	766.4	5.84	6.66	+14	9.90	9.80	-1
Zn	213.8	0.93	0.85	-9	0.054	0.047	-13

TABLE 4-67. RANGE OF RECOVERIES FOR FERTILIZER STANDARDS

Element	Range of recoveries, %	Concentration range, %
B	96 to 103	0.04 to 28.4
Ca	93 to 100	2.1 to 13.4
Cu	82 to 125	0.01 to 8.9
Fe	78 to 134	0.37 to 0.78
Mg	83 to 109	0.45 to 14.5
Mn	87 to 106	0.09 to 3.95
P[a]	97 to 105	4.3 to 47.5
K	90 to 106	6.5 to 53.8
Zn	86 to 105	0.05 to 0.89
P[b]	95 to 107	4.2 to 28

[a] By digestion.

[b] By citrate extraction.

sample to be in a liquid form prior to analysis. Clearly, the choice of sample preparation procedures for ICP/DCP determinations is highly matrix- and target-element specific. The greater the coverage of elements that is desired, the less flexible will be the preparation regimen available to the analyst. In all but the most simple samples, the sample preparation procedures will exclude certain elements or groups of elements from determination.

4.4 SAMPLE INTRODUCTION TECHNIQUES

Sample introduction and preparation condition the sample before it enters the plasma and thus, are significant factors in determining the accuracy of the analysis (Browner and Boorn 1984a).

The goals of sample introduction into the ICP or any other excitation source are the reproducible transport of the sample material to the source with high efficiency and with no adverse interference effects (Browner and Boorn 1984a).

Sample introduction into the ICP requires that a desolvated stable aerosol or gas be produced by the sample introduction system. The type system that should be used depends on whether the sample is liquid, solid, or gaseous; on the quantity of sample available; and on the type number and concentration of elements of interest in the sample.

Barnes (1978) has shown schematically (Figure 4-5) some of the possibilities for sample introduction into the ICP. Only one of these, conventional pneumatic nebulization of dilute aqueous or nonaqueous liquids, has been shown to be capable of providing a sample for the plasma suitable for multielement determination for a wide variety of elements and matrices. The generation of volatile metal hydrides for introduction into the ICP also has been shown to be successful for a limited number of elements, but there are many problems with this application that detract from its usefulness as a multielement sample introduction technique. Other techniques such as ultrasonic nebulization; electrothermal vaporization systems; and the use of filaments, sparks and conventional nebulization systems for the direct or indirect introduction of solids, powders, or slurries have not proven commercially acceptable and have shown the capability to provide stable aerosols for only a limited number of elements. A brief description and review of these sample introduction techniques is provided in the following sections.

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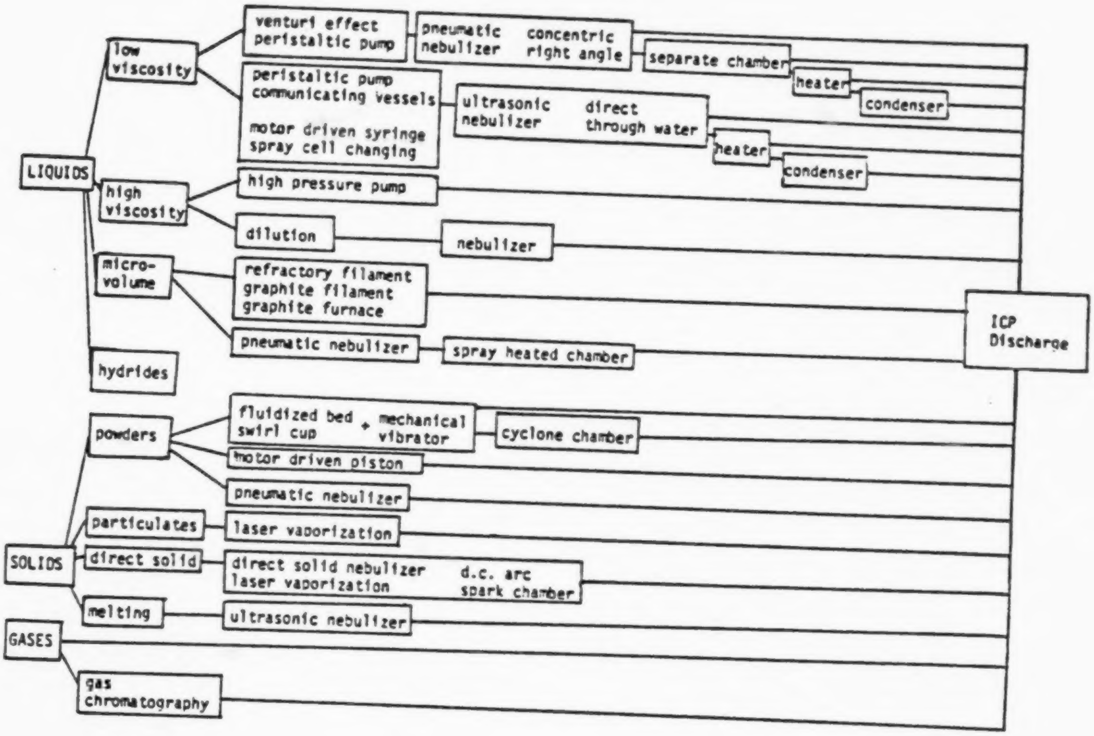
LIQUIDS
low viscosity
venturi effect
peristaltic pump
pneumatic nebulizer
concentric
right angle
separate chamber
heater
condenser
peristaltic pump
communicating vessels
motor driven syringe
spray cell changing
ultrasonic nebulizer
direct through water
heater
condenser
high viscosity
high pressure pump
dilution
nebulizer
micro-volume
refractory filament
graphite filament
graphite furnace
pneumatic nebulizer
spray heated chamber
hydrides
ICP Discharge
SOLIDS
powders
fluidized bed
swirl cup
+
mechanical vibrator
cyclone chamber
motor driven piston
pneumatic nebulizer
particulates
laser vaporization
direct solid
direct solid nebulizer
laser vaporization
d.c. arc
spark chamber
melting
ultrasonic nebulizer
GASES
gas chromatography

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Figure 4-5. ICP sample introduction techniques.

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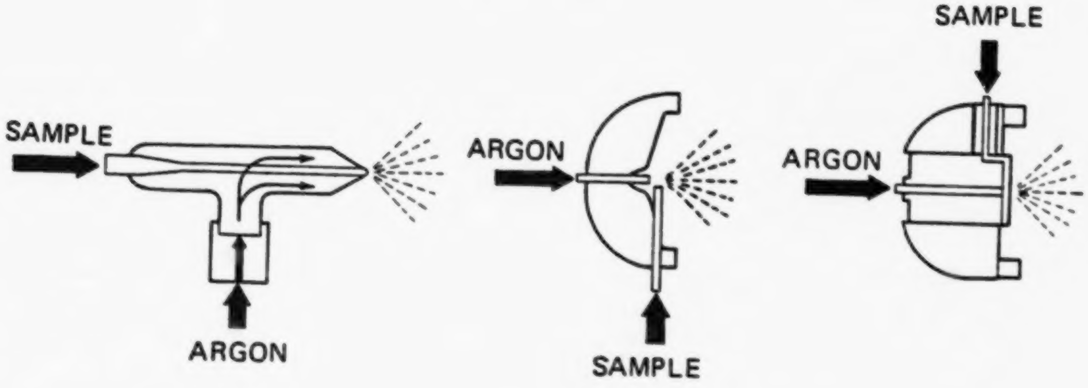
4.4.1 Introduction of Aqueous Liquids via Nebulization

Aqueous liquid samples available in more than 1-mL quantities are generally introduced into the plasma by means of a nebulizer spray-chamber system with the aid of a peristaltic pump that segments the sample into drops and forces them through a glass or quartz nebulizer capillary into a spray chamber. The droplets then are shattered either by an obstruction in the spray chamber or by a cross flow of argon (Kahn et al. 1979b). The result is the formation of aerosol particles of a wide range of diameters. Those above a certain critical diameter pass out of the spray chamber as waste. The smaller particles are carried upwards into the plasma by the aerosol-carrier argon gas flow where they are desolvated, decomposed, and atomized. This approach to sample introduction is termed pneumatic nebulization and is the most popular approach used in ICP spectroscopy.

Pneumatic nebulization of liquids is very inefficient. Typically, no more than 1 percent of the sample is transported into the plasma. The actual efficiency of aerosol transport cannot be calculated accurately.

There are four basic types of pneumatic nebulization systems used in ICP-AES. The concentric, or Meinhard, nebulizer and the cross-flow nebulizer (Figure 4-6) are the two most commonly used pneumatic nebulizers, with the Babington high-solids nebulizer used less frequently. The concentric nebulizer is subject to blockage by particulates and, because it is generally made of glass, is subject to attack by hydrofluoric acid. The cross-flow nebulizer can accept higher concentrations of dissolved solids and often is available in acid-resistant polypropylene. The Babington nebulizer can also accept high dissolved-solids concentrations, up to 10 percent, but above this level the tip of the sample introduction tube tends to clog. Thus, the limiting factor for dissolved-solids concentrations is the torch aerosol-carrier tube and not the design of the pneumatic nebulizer (Allied Analytical Systems 1986).

An often overlooked aspect of sample introduction via nebulization is the contribution of the spray chamber (Figure 4-7). Its function is to trap the larger sample aerosol droplets generated by the nebulizer. A pneumatic nebulizer typically will generate aerosol droplets of 30-μm mean diameter while the optimal size for introduction into the plasma is around


SAMPLE
ARGON
ARGON
SAMPLE
SAMPLE
ARGON

CONCENTRIC CROSS-FLOW BABINGTON

Figure 4-6. ICP nebulizers © 1986, courtesy of Allied Analytical Systems.

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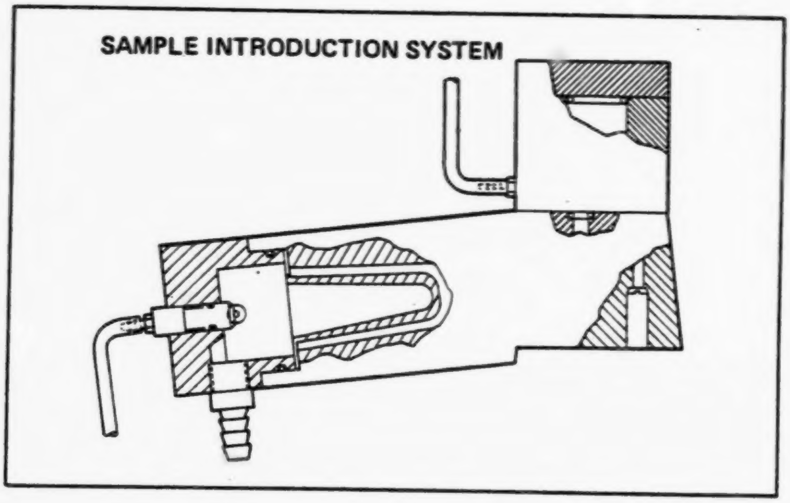
SAMPLE INTRODUCTION SYSTEM

Figure 4-7. Spray chamber nebulizer system © 1986, courtesy of Allied Analytical Systems.

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5 μm (Allied Analytical Systems 1986). The most significant aspects of the spray chamber are its cutoff diameter, a measure of the effectiveness of aerosol modifiers within the chamber of removing drops of a certain size, and its washout time, generally defined as the time required for a drop to 0.1 percent of the emission intensity level of the previous sample when nebulizing a blank solution. Typical washout time for ICP spray chambers are around 20 to 45 s and need to be monitored closely when analyzing samples of widely varying concentrations in the same analysis period. Dobb and Jenke (1983) observed that the primary source of the memory noted for typical pneumatic nebulizers is the dissipation rate of the fog produced by the nebulizer during introduction of the previous sample. They developed a mathematical correction for this effect. Ramsey et al. (1983) found that the dead volume of the nebulizer also contributed to sample washout time and developed a modified nebulizer with less dead volume. One reason why pneumatic nebulizer systems are the most widely accepted sample introduction systems is that, because most users regard ICP-AES as an alternative to flame atomic absorption, they are only concerned about liquid samples at 0.1- to 1-mg/L levels. Thus, solid sample and ultrasonic nebulizer modes of introduction are of no use to these users.

There are disadvantages of pneumatic nebulizers and spray chambers:

- The solution uptake rate is a function of sample viscosity.
- Samples with high dissolved-solids content can block the nebulizer orifice.
- Sample volumes greater than 1 mL are needed.
- Long washout times for the spray chamber.
- Depending on the composition of the nebulizer and the type samples introduced, sample contamination can occur. Glass nebulizers can contribute B, Si, and Na; stainless steel Cr, Ni, and Fe; and sapphire or alumina, Al.

Whereas pneumatic nebulization systems have gained commercial acceptance, ultrasonic nebulization has remained primarily a research tool.

Both batch- and continuous-feed ultrasonic nebulization systems have been used (Olson et al. 1977). In batch systems, the ultrasonic energy is applied to a fixed volume of sample solution, either directly through an inert liquid, or indirectly through a solid interface. In continuous-feed systems, the sample solution is continuously pumped onto the ultrasonic transducer plate. The ultrasonic energy produces a sample aerosol, which generally must be desolvated prior to its introduction into the plasma. If the sample is not desolvated, solvent concentration in the plasma may reach unacceptably high levels, which can result in quenching of the plasma. The most significant advantage of the ultrasonic nebulizer over a pneumatic system is that lower detection limits (often a factor of 10 or lower) can be achieved due to the increased concentration of analyte in the plasma. Table 4-68 shows the typical improvement in detection limits for selected standard solutions of elements introduced into an ICP through an ultrasonic nebulizer.

There are other advantages of ultrasonic nebulizers over pneumatic nebulizers (Olson 1977).

- Because the rate of aerosol production at the transducer is independent of argon carrier-gas flow, the aerosol production rate and the carrier-gas flow rate may be varied independently to optimize analytical performance.
- Ultrasonic nebulizers can produce aerosols of greater number, density, and more uniform particle size.
- Because the mean particle size is frequency dependent, smaller particles can be produced by increasing the ultrasonic frequency. The smaller the particle, the more efficiently it is transported, desolvated, atomized, and excited.

Disadvantages of ultrasonic nebulizers are:

- A substantially higher cost than that of commercially available pneumatic systems
- Corrosive agents present in the solvent often attack the transducer
- Memory effects
- Inconvenient sample size capability
- Dissolved-solids concentrations can cause variations in aerosol production rates
- Requires a separate power supply

TABLE 4-68. COMPARISON OF DETECTION LIMITS FOR ULTRASONIC AND PNEUMATIC NEBULIZERS (μg/L)

Element	Pneumatic	Ultrasonic
[a]		
Al	4	0.4
As	20	2
Cd	2	0.07
Co	2	0.1
Cr	0.9	0.08
Cu	0.8	0.04
Fe	4	0.5
Mn	0.1	0.01
Mo	4	0.3
Ni	8	0.3
Pb	10	1
Se	10	1
V	2	0.09
Zn	3	0.1
[b]		
Mn	2	1
Cu	27	7
Zn	25	5
Co	12	3
Pb	84	7
Cd	16	2
Fe	4	2
Ni	14	2
Cr	5	2
V	5	4
[c]		
Ag	5	0.8
Al	40	3
As	60	6
B	9	4

Footnotes at end of table.

(continued)

TABLE 4-68 (continued)

Element	Pneumatic	Ultrasonic
c (continued)		
Ba	0.3	0.09
Be	0.2	0.04
Bi	50	9
Ca	6	2
Cd	5	0.3
Co	6	0.4
Cr	5	0.3
Cu	3	0.8
Fe	2	0.2
Hg	15	4
Mg	30	3
Mn	4.5	0.08
Mo	12	2
Na	1500	240
Ni	30	1
Pb	30	2
Sb	50	4
Se	600	3
Sn	60	4
Sr	0.06	0.03
Te	50	1
Th	12	1.3
Ti	2	0.2
Tl	75	20
V	2	0.3
Y	0.8	0.08
Zn	8	0.8

[a] From Olson et al. (1977).

[b] From Berman et al. (1980).

[c] From Taylor and Floyd (1981).

- Interferences are greater, requiring sample dilution, thus reducing any gain in sensitivity achieved
- If low detection limits are to be achieved, desolvation of the sample is required, hence an extra step in the sample introduction process is required.

Taylor and Floyd (1981), noting the limitations of pneumatic nebulizers in meeting the detection limits of the EPA Primary Drinking Water Standards for 8 elements, developed an ultrasonic nebulizer system capable of determining these elements at maximum contaminant levels (Table 4-69).

Berman et al. (1980) used an ultrasonic nebulizer to introduce desolvated metal concentrates from seawater into an ICP. Ultrasonic nebulization was found to be necessary, because even a 20-fold preconcentration of most metals of interest in seawater is not sufficient for the detection limits of a conventional nebulization system.

4.4.2 Introduction of Nonaqueous Liquids Via Nebulization

While many of the same factors that determine the efficiency and suitability of pneumatic nebulizers and spray chambers to handle aqueous liquids also apply to organic liquids, there are some significant differences that must be noted. The most important of which are that the viscosity of organic solvents differs from that of water and they are much more volatile. The result is that the rapid evaporation of organics will result in a much higher transport efficiency than is observed with water and thus a much higher loading of the plasma. This may extinguish the plasma or reduce its excitation properties. For example, the transport efficiency of water with a cross-flow nebulizer is around 1.5 percent whereas efficiences for organic solvents are much higher: benzene (27 percent), xylenes (14 percent), and nitrobenzene (15 percent) (Browner and Boorn 1984a). This also requires increased forward power to the ICP to decompose the organics beyond that which would be required if the organics had transport efficiency identical to water (Kahn et al. 1979a; Browner and Boorn 1984b).

There are also practical problems with the analysis of organic liquids by nebulization. If the same system is used routinely for both aqueous and nonaqueous sample introduction, the spray chamber must be thoroughly dried

TABLE 4-69. MAXIMUM CONTAMINANT LEVELS FOR INORGANIC CHEMICALS IN DRINKING WATER AND ICP DETECTION LIMIT DATA

		ICP nebulizer			
		Pneumatic		Ultrasonic	
Contaminant	Maximum level (mg/L)	DL[a] (mg/L)	LQD[b] (mg/L)	DL[a] (mg/L)	LQD[b] (mg/L)
Arsenic	0.05	0.06	0.210[c]	0.006	0.020
Barium	1	0.003	0.009	0.00009	0.0003
Cadmium	0.05	0.005	0.015	0.0003	0.001
Lead	0.05	0.030	0.100[c]	0.002	0.005
Mercury	0.002	0.015	0.050[c]	0.004	0.015[c]
Selenium	0.01	0.060	0.300[c]	0.003	0.010
Silver	0.05	0.005	0.025	0.0008	0.0025

[a] Detection limit (DL) is three times the standard deviation of background emission.

[b] Lowest quantitative determinable concentration (LQD) is 10 times the standard deviation of background emission.

[c] Underscored values indicate LQD exceeds maximum contaminant level concentration.

or otherwise flushed out prior to introduction of organic solvents immiscible with water and vice versa. Organics also tend to build up carbon deposits on the tip of the sample introduction tube of the torch.

4.4.3 Introduction of Solids, Slurries, and Microliter Samples

Various approaches to the direct introduction of solids into the plasma have been attempted. The obvious advantages of the development of a successful solid-sample introduction system would be avoiding sample-dissolution steps and the resulting increase in the sensitivity for the elements of interest. The approach has suffered from several general shortcomings that have limited its application to researchers although certain newer instruments are claimed to be equipped with this capability. The first problem is the difficulty in generating particles of uniformly small size (F5-10 mm in diameter) that can be representatively transported into the plasma. The second problem is one of spectral interferences from the high background associated with these particles. This often requires another step to separate the background contributing elements and thus complicates the procedure. The studies summarized below indicate the status of this approach to sample introduction.

The most primitive means of sample introduction into a plasma source resembles that employed in SSMS. Such a system has been described by Human et al. (1976) and by Scott (1978). This system uses a spark discharge between two graphite electrodes situated above a powder sample to generate fine particles from the sample. The particles are swept into the plasma by argon gas fed through the spark chamber at 1 L/min. The electrode assembly, which is situated directly below the torch, replaces the nebulizer and spray chamber of a conventional commercial system. The sample must be either a conducting material or in a conducting matrix such as graphite. This approach suffers from high detection limits (2 to 150 ppm for Cu, Mg, and Zn in Al alloys) and long analysis times. The long analysis times result from the extensive prepacking required to achieve stability of particle generation. The apparent advantage of this approach is that sample preparation need not be extensive.

Farnsworth and Hieftje (1983) described a method of sample introduction for ICP-AES that also closely resembles that employed in SSMS. Instead of the sample being transported to the plasma, the plasma is brought to the sample by a grounded conductor placed below the sample tube of a modified ICP torch. When the plasma is ignited, it produces a radio frequency arc from the conductor to the sample, vaporizing some of the sample that is carried into the plasma. The approach suffers from numerous drawbacks including the introduction of unusually large fluxes of matrix or minor constituent elements into the plasma resulting in nonlinearities in plasma emission, severe line broadening, and background shifts; fractional time-dependent distillation of components; the need for total sample consumption; and irreproducible transient signals. These problems were evident in the analyses of alloys, NBS SRM 1633 coal fly ash, and microliter aqueous samples, all of which required unique sample containment prior to the sample introduction.

The use of a laser microprobe to vaporize solid samples prior to plasma introduction has been described by Thompson, Goulter, and Sieper (1981) for analysis of homogeneous steel samples. Detection limits were substantially higher for the laser-ICP microprobe when compared with nebulization on the same ICP instrument:

	μg/g in steel	
Element	Laser	Nebulizer
Cr	15	2
S	15	45
P	10	35
Mn	80	2
Mo	60	4.5
Cu	20	1.5
V	10	1.5
Ni	70	1.0

Attempts to analyze heterogeneous rock samples by this method proved unsuccessful, producing particles that were too large to be volatilzed effectively in the plasma.

Thermal atomization of aqueous samples from tantalum filaments (Nixon et al. 1974) or from graphite rods (Kirkbright et al. 1980; Gunn et al. 1978; Millard et al. 1980) followed by direct introduction of the atoms into the plasma source has been explored as an alternative to pneumatic nebulization.

The graphite-tube ICP interface, as described by Kirkbright et al. (1980), consists of a graphite rod enclosed in a glass chamber, which is connected to the central tube of the torch by plastic tubing. Samples are first desolvated and then vaporized by application of preprogrammed heating cycles to the graphite rod. The vaporized sample then is carried into the plasma on a continuously flowing stream of argon passing through the glass chamber.

The analogy of this mode of sample introduction to graphite furnace atomic absorption has been made; however, there are fundamental differences in the role played by the graphite rod in the ICP system. First, close control of the final vaporization temperature is not as critical as in AAS. This is because the sample atomization and excitation (for ICP emission) stages occur in the plasma. The graphite rod is only needed to release a reproducible pulse of sample into the plasma, whereas in atomic absorption the rod or furnace must both vaporize and atomize the sample.

Gunn et al. (1978) used 2400 °C for their analyses using the graphite tube and determined detection limits for 16 elements in terms of analyte concentration for a 10-mL aqueous sample. Detection limits were defined as twice the noise level in the plasma background emission. The detection limits are compared with those for the tantalum filament in Table 4-70.

For most of these elements, the graphite-rod system provided lower detection limits. The precision of 15 repetitive injections of 10-mL aliquots of 400-mg/L solutions of the elements was around 5-percent RSD.

The primary advantage to these methods of sample introduction is that the detection limit is lowered because of increased analyte concentrations in the plasma. Another advantage is that smaller sample volumes, typically 10 to 100 mL, can be used.

TABLE 4-70. COMPARISON OF DETECTION LIMITS (µg/L) FOR GRAPHITE TUBE-ICP WITH TANTALUM FILAMENT-ICP SAMPLE INTRODUCTION

Element	Graphite tube	Tantalum filament
Ag	0.1	1
As	200	100
Au	--	--
Be	0.1	0.2
Cd	3	60
Ga	1	--
Hg	6	20
In	2	--
Li	0.4	--
Mn	0.1	--
P	20	20
Pb	10	30
Re	10	--
Sb	30	10
Tl	6	30
Zn	2	--

The limiting factor with graphite-rod sample introduction is possible interferences present in the sample that may hinder the rate of analyte vaporization and transport into the plasma. Millard et al. (1980) investigated this problem for Cd and As finding that Se(VI) was needed to improve the sample transport efficiency of Cd.

Preliminary work by Salin and Horlick (1979) has demonstrated the possibility of directly inserting powders, solids, or desolvated liquids into the core of the plasma, eliminating the need for complicated sample-introduction systems. The sample container is a conventional undercut cup graphite electrode commonly used in DCP-AES; however, attempts to analyze solid Spex G standards, NBS coal SRM 1632, and NBS orchard leaves SRM 1571 were inconclusive both with respect to identification and quantitation of elements.

Z. Li-Xing et al. (1983) described a microprocessor-controlled graphite-rod-direct-insertion device. The insertion of the rod or graphite cup into the plasma is effected by a microprocessor-controlled stepper motor assembly. The software design enables the plasma to be used for the desolvation and ashing of sample solutions as well as for their vaporization. Positioning of the rod is critical during each stage (dry, ash, atomize) and optimum conditions must be determined on an element- and matrix-specific basis. Manganese in 5-percent glucose was determined at the 50-ppb level using this system.

Ng et al. (1984) described a powder injection device in which a tangential argon flow created inside the device mixes and carries the powder (0.5 to 2.5 ng) into the ICP. Sample sizes smaller than 0.5 ng give emission intensities that are too low to quantitate, and those greater than 2.5 ng do not properly dissociate in the plasma. The technique was applied to the determination of six elements in NBS SRM 1033 coal ash. The precisions observed for 5 consecutive measurements ranged from 5- to 12-percent RSD for Cr, Sr, Ti, V, Cu, and Zn all present at levels from 100 to 8000 ng/g. Detection limits ranged from 2 to 7 ng.

Ng and Caruso (1983) converted Zn, V, U, and Cr, known refractory elements, to their chlorides in an electrothermal carbon cup by the addition of ammonium choride. The elements were then subjected to an electrothermal vaporization program of drying, ashing, and vaporization, after which they were swept into the ICP. The precision was around 6-percent RSD over a linear range of 0.1 to 10 ppm.

Kirkbright and Li-Zing (1982) used a different approach to determine refractory carbide-forming elements by electrothermal vaporization into an ICP. The use of 0.01-percent Freon in an argon carrier-gas mixture converted these elements to volatile fluorides. The sample solutions (5 µL) were applied to the top of a graphite rod, desolvated with a heat gun, and manually raised into the plasma. Detection limits improvements over injection without the Freon gas were a factor of 100 times better for U, Zr, and Ti (Table 4-71).

Kitazume (1983) vaporized a 10-µL sample solution of B, Ge, P, Pb, Sn, and Zn on a Pt or W filament at 1400 °C and introduced the vapor into the ICP through a 5-mL evaporation chamber above the sample. The typical evaporation-chamber size for the graphite rod approach is 100 mL. Detection limits ranged from 1 to 10 µg/L. Precisions of 2- to 10-percent RSD were observed for 1 mg/L solutions.

Rica and Kirkbright (1982) and Barnett et al. (1983) determined Ni in freeze-dried milk by electrothermal vaporization into an ICP. Unless the sample was first digested in acid and extracted into dithizone, the high spectral background that resulted reduced the sensitivity significantly.

Sugimae and Mizoguchi (1982) collected air-particulate matter on polystyrene fiber filters, dissolved the filters in xylene, and directly nebulized the suspensions into an ICP through a conventional concentric glass nebulizer. Although the nebulizer capillary is small, 0.5 mm i.d., the particles present on the dissolved filters did not clog it. The ICP was calibrated with a xylene suspension of NBS SRM 1648 urban particulate matter. Levels of Fe present (1 to 3 mg/L) in the suspension produced RSD's of 5 percent for 6 separate 10-s integrations.

Fuller et al. (1981) nebulized slurries of silicate rocks into an ICP using a cross-flow nebulizer modified to accept up to 10-percent solids. The samples must be ground to a particle size of less than 10 µm and be homogeneously distributed within the solution. The precision observed for Zr was 0.02-percent RSD.

TABLE 4-71. ANALYTICAL WAVELENGTHS EMPLOYED AND DETECTION LIMITS OBTAINED

Element	Wavelength/nm	Detection limit(ng)		
		Without injector gas	Argon as injector gas	Ar-Freon injector gas
U	385.96	700	290	1.9
Zr	343.82	—[a]	—[a]	1.1
Ti	334.94	140	110	0.89
Mo	313.26	4.4	6.3	1.0
B	249.77	1.7	2.0	1.3
Cr	357.87	0.024	0.021	0.020
Ag	328.07	0.0023	0.0023	0.0018
Cu	324.75	0.0098	0.011	0.0073
Zn	213.86	0.0035	0.004	0.004

[a] Even using a 5,000-ng sample no signal was observed.

The results of analyses of silicate rocks and ores using this method are given in Tables 4-72 and 4-73.

4.5 ELEMENT IDENTIFICATION AND QUANTITATION

4.5.1 Analysis Procedures and Detection Systems

An ICP-AES analysis is generally carried out by the nebulization of the liquid sample into the plasma. The emission produced by the sample elements is then observed by a spectrometer system. The sample is nebulized for a fixed time period, generally 20 to 45 s, during which the plasma is conditioned by the sample and the sample emission lines of interlap are recorded by the detection system. Prior to sample analysis, the entire system is standardized by the analysis of 1 to 3 calibration standards. Several different multielement mixtures are used to avoid potential chemical interferences which might result if one mixture was prepared containing all elements. The time spent by the spectrometer on a particular wavelength is referred to as the integration time and is generally around 10 to 15 s.

There are two basic spectrometer system designs. The earliest ICP spectrometers were of the fixed wavelength or simultaneous design, also called a direct reader. The diffraction grating used to disperse the emission from the ICP torch is fixed in position within the spectrometer. The dispersed light is then detected by separate photomultiplier tubes after passage through fixed exit slits arranged along the focal plane of the spectrometer. Only those wavelengths of light that are diffracted and focused onto these exit slits are detected. To determine additional elements or to measure emission at other wavelengths, additional exit slits must be included. This is generally very costly and there are physical limitations to the number of exit slits that can be added. The earliest direct reading or polychromator systems did not have the capability to observe the emission on either side of the wavelength of interest. Thus, any interfering wavelengths or spectral background effects could not be corrected conveniently. Newer polychromators have either quartz refractor plates, moveable exit slits, or monochromator systems that can be used to correct for spectral background. The advantage of the polychromator system is that all of the elements for which there are exit slits and photomultiplier tubes (PMT's) are determined simultaneously. Most polychromators have between 20 to 35

TABLE 4-72. DETERMINATION OF TRACE ELEMENTS IN STANDARD USGS SILICATE ROCKS USING ICP ATOMISATION

Sample No.	Concentration (μg/g)													
	Ti		Zr		Ba		Cr		V		Y		Mn	
	Found	Certified	Found	Certified	Found	Certified	Found	Certified	Found	Certified	Found	Certified	Found	Certified
2514	1,900	2,000	120	120	70	80	3,200	3,400	60	65	10	5	1,000	1,400
2515	10,500	11,600	130	150	110	90	170	205	300	320	30	22	1,500	1,400
2266	13,000	12,000	130	200	250	290	570	630	170	180	10	--	1,000	1,400
2487	15,000	13,000	140	180	60	66	75	77	220	200	10	--	1,500	1,700

TABLE 4-73. DETERMINATION OF TRACE ELEMENTS IN RUTILE ORES USING ICP ATOMISATION

Sample	Concentration (μg/g)											
	Al		Cr		Mn		Nb		V		Zr	
	Found	Certified	Found	Certified	Found	Certified	Found	Certified	Found	Certified	Found	Certified
A	800	800	100	90	25	30	2,500	2,900	3,000	3,500	2,800	3,500
B	700	800	120	90	30	40	2,600	2,800	5,000	5,600	4,600	4,900

exit slit/PMT's or channels. Polychromators are best suited for routine analyses of samples of known interference characteristics and elemental composition.

The analysis of samples using a polychromator system requires that compromise conditions be established; that is, the gas flows, observation height above the load coil, integration times, and power to the load coil must all be fixed during the analysis, and thus represent a compromise of all conditions to maximize the detectability of the elements of interest.

The use of a monochromator or sequential scanning spectrometer does not require that compromise conditions be established for a group of elements. Instead, the grating is rotatable by means of a computer-controlled stepper motor and the dispersed wavelengths are focused onto a single exit slit and detected by a single PMT. The individual wavelengths of interest are observed sequentially according to programming instructions supplied to an instrument-dedicated minicomputer. The advantage of this approach is that all elements and all wavelengths theoretically can be determined in the same sample. In reality, the number of elements determinable at a single analysis session is limited by the amount of sample available (a nebulization rate of 1 mL/min and an analysis time of around 1 min per element imposes limitations on the number of analyses that can be performed) and the capability of the grating to locate reproducibly the wavelengths of interest.

4.5.2 Data Processing

The emission-line intensities recorded by the PMTs are converted to electrical signals and recorded by the minicomputer as counts per second. The results are compared to the calibration curve stored within the computer and are printed out as a hard copy and stored, if desired, on magnetic tape or hard disk for archiving. Newer spectrometers are equipped with sophisticated graphics capabilities including the ability to display several spectra at once, carry out spectral subtractions, and select alternate wavelengths from a computerized data base.

4.6 ELEMENTAL COVERAGE

Marketing literature and some published articles have quoted coverage capability for plasma spectroscopy (ICP-AES) of 60 elements in a single analysis of a single sample. In this section, the documented capability of ICP-AES to carry out a qualitative, semiquantitative, and quantitative survey analysis of sample is addressed.

4.6.1 Determination of Radioactive Elements

As noted, of the 22 naturally radioactive elements, most are not likely to be found at chemically detectable levels in environmental sample matrices.

A review of the literature disclosed only the determination of U and Th by ICP-AES. Thus, the capability of ICP-AES to determine radioactive elements has not been established (Table 4-74).

One problem that confronts analysts proposing to analyze samples that may be contaminated with radioactivity is that of containing the radiation. Lautensleger and Hara (1984) discussed the necessary modification to a commercially available ICP for application to radioactive analyses. The system was designed to limit operator exposure levels. First, a simultaneous system was selected to keep sample volumes low and to otherwise limit exposure potential. A lead-shielded glove-box containment was interfaced between the spectrometer and the source stand. Extensive modifications were necessary, including mounting of the gas control system outside the source stand and using an autosampler. No data on analyses of radioactive samples were presented.

4.6.2 Determination of Nonmetals and Gases

Of the 16 elements identified as nonmetals and gases, only two, P and B, have been determined quantitatively on a routine basis by plasma spectroscopy.

No data could be found for the determination of H, He, Ne, Kr, Xe, and Ar by plasma spectroscopy.

Several authors have investigated the potential for determining carbon, nitrogen, oxygen, fluorine, bromine, iodine, chlorine, and sulfur by ICP methods. In most cases, these efforts have been limited to a preliminary characterization of the primary emission lines for these elements. Most of the environmental applications have been limited to gas-phase analyses and, even then, under severe restrictions (e.g., the total light path from the

TABLE 4-74. DOCUMENTED SINGLE-OR MULTIELEMENT COVERAGE CAPABILITY OF ICP-AES FOR NATURALLY RADIOACTIVE ELEMENTS

Element	Qualitative	Quantitative	Unacceptable or unknown
Astatine			X
Francium			X
Technetium			X
Polonium			X
Promethium			X
Radon			X
Radium			X
Actinium			X
Thorium		X	
Protactinum			X
Uranium		X	
Neptunium			X
Plutonium			X
Americium			X
Curium			X
Berkelium			X
Californium			X
Einsteinium			X
Fermium			X
Mondelivium			X
Nobelium			X
Lawrencium			X

torch to the monochromator or polychromator must be purged of atmospheric oxygen or the optical path must be evacuated). This is necessary because oxygen has strong molecular absorption bands below 190 nm, the region in which the most sensitive emission lines for these elements are found (Heine et al. 1980; Wallace et al. 1980). Although several commercial instruments have the capability to operate in either the purged or evacuated mode, few documented applications have been described. Most of these applications involved the use of homemade systems specifically modified to handle vacuum or purge conditions.

Northway et al. (1980) investigated atomic nitrogen lines when gaseous nitrogen compounds were introduced as samples. Argon was used as a purge gas. Nitrogen at ppm levels in welding-grade argon was determined using a 157-µL Teflon gas-sampling loop. Northway and Fry (1980) investigated the determination of oxygen at microgram levels in gas samples by using atomic oxygen lines, and Brown and Fry (1981) studied near-infrared atomic oxygen emissions derived from permanent gases and volatile organic liquids. The detection limit reported for oxygen was 25 ng for direct gas-sample injections into the ICP. Hughes and Fry (1981a) reported on atomic emission lines for chlorine and bromine in the near infrared using air path instrumentation. The reported detection limit for both bromine and chlorine was 0.05 µg for 8-µL gas sampling loop injections of HBr and Cl_2 into a low-volume transfer line leading directly into the ICP. Fry et al. (1980) reported on ICP atomic emission lines of fluorine for the region 350 to 895 nm using the test compounds SF_6, CF_4, CCl_2F_2, and ClF_2CCF_2Cl. The detection limit was 0.35 µg for direct gas-sampling-loop injections. Hughes and Fry (1981b) studied near-infrared atomic emission lines of sulfur and carbon (>900 nm) using 8-µL gas-sampling-loop injections of H_2S and CH_4. The detection limits were 0.006 µg for sulfur and 0.13 µg for carbon. Wallace (1980) measured sulfur in an aqueous solution of 10-µg/mL K_2SO_4 at a detection limit of 0.05 µg/mL at 180.73 nm after the optical path was purged with nitrogen.

Ward and Marciello (1978) discussed the determination of sulfur, carbon, phosphorus, and iodine in aqueous and oil matrices by ICP-AES using a simultaneous detection system. Variable background from sample to sample was found to be a major problem in nonmetal determination and was corrected for by using a stepping refractor plate to produce wavelength scans near the analytical lines. High-carbon blanks were found to be caused by hydrocarbons, CO_2, and CO in the argon plasma. Detection limits, precision, and results of analyses of solutions containing known concentrations of carbon and sulfur are shown in Tables 4-75 through 4-78. The detection limit was defined as the concentration required to give a signal equal to twice the standard deviation of the blank on a set of 10 replicates for both aqueous and xylene solutions.

Miles and Cook (1982) determined sulfate as sulfur in groundwater samples by ICP by using the third-order 180.73-nm line. A homemade argon purge system operated at 1.5 L/min was used to remove oxygen from the light path between the plasma and the spectrometer. It consisted of an open quartz tube extending from the primary optics to within 2 cm of the torch. The acid used to preserve water samples (1 percent HCl) caused a decrease in sulfur emission intensity and required that the acid content of standards and samples be the same. A weak calcium line at 180.734 nm partially overlapped the sulfur line such that 1000 mg/L Ca produced a signal equivalent to 25 mg/L as sulfate. This required that calcium be measured in all samples as well, so that the apparent sulfate concentration as calcium could be subtracted. The short-term precision, as defined by 20 successive 10-s integrations, was 0.8-percent RSD for 200 mg/L sulfate and 1.2-percent RSD for 2,800 mg/L sulfate in seawater. The detection limit, based on measurement of the background signal, was 79 µg/L as sulfate.

A comparison of results by the ICP procedure and an automated spectrophotometric procedure gave a correlation coefficient of 0.99 over the range 10 to 300 mg/L for rainwater and groundwater. The analyses of sulfate in certified reference materials gave the following results:

Reference Material	ICP	Certified value as sulfate in mg/L	% Bias
EPA QC Sample	7.3	7.2	+1
IOS Standard Seawater	2800.0	2781.0	+1

Because these investigations are, at best, of a preliminary nature and because no routine applicability has been demonstrated, it is concluded that plasma methods cannot provide satisfactory analytical determinations

TABLE 4-75. DETECTION LIMITS FOR NONMETALS (mg/L)

Element	Water	Xylene
Carbon	1.00	--
Iodine	0.10	--
Phosphorus	0.03	0.05
Sulfur	10	50.00

TABLE 4-76. PRECISION OF ICP FOR NONMETALS (% RSD) (WATER)

Concentration (mg/L)	RSD (%)			
	Carbon	Iodine	Phosphorus	Sulfur
1	52	6	5	--
10	7	4	3	45
25	3	3	1	21
50	4	3	1	13
100	2	2	1	9
250	3	2	--	--
500	1	--	--	--
1,000	1	--	1	1

RSD = Relative standard deviation.

TABLE 4-77. PERCENT RECOVERY OF CARBON IN WATER BY ICP-AES (mg/L)

Expected	Measured	Percent recovery
0.2	<1	--
10.0	8.9 ± 2.7	89
15.0	13.9 ± 1.8	93
20.0	20.7 ± 2.3	104
300.0	302 ± 9	101
400.0	418 ± 38	105

TABLE 4-78. PERCENT RECOVERY OF SULFUR IN NBS-SRM 1634 FUEL OIL

Expected	Measured	Percent recovery
2.14 ± 0.02	1.9 ± 0.5	89

of nonmetals and gases (excluding P and B) in environmental samples (Table 4-79.

4.6.3 Determination of Noble or Precious Metals

Researchers have shown little interest in the determination of noble or precious metals by plasma spectroscopy. This is perhaps because the naturally occurring levels of these elements are below ICP/DCP detection limits except in a few ores and minerals. Except for the two regulated elements Ag and Os, the other elements Ir, Pt, Au, Pd, Ru, and Rh have received little attention although their analysis is feasible by ICP-AES. The majority of reported applications have dealt with determination of operating conditions for purposes of demonstrating determination capability rather than analysis of environmental samples.

Kirkbright and Tinsley (1979) conducted studies to establish optimum operating conditions for the simultaneous determination of noble metals in water. Detection limits, wavelengths, and observation heights were determined (Table 4-80). The effect of the other noble metals at 100 ppm on 10-ppm solutions of individual noble metals was not greater than ±5 percent, except for Ru, which enhanced the Pt signal by 51 percent. The similar effect of 1,000-ppm Na, Fe(III), Ni, Cu, and Zn on the same solution was typically ±5 percent.

Barnes (1978), Boumans (1979), and Reednick (1979) also determined compromise conditions for analysis of noble metals in water (Table 4-80).

The Environmental Monitoring Systems Laboratory's (EMSL-RTP) protocol for the analysis of metals collected on air filter particulates (U.S. EPA 1981a) employs a simultaneous system with channels for noble metals, because their goal is a complete characterization of metals on air particulates. Lower limits of quantitation and upper limits sought are shown in Table 4-81.

Weymss and Scott (1978) reported detection limits for noble metals in aqueous solution as part of a study for determination of these elements in ores and related plant materials. No environmental applications data were given.

Jones (1978) used a simultaneous ICP-AES system to determine Pt in soil extracts and plant tissue ash solutions.

TABLE 4-79. DOCUMENTED SINGLE- OR MULTIELEMENT COVERAGE CAPABILITY OF ICP-AES FOR NONMETALS AND GASES IN ENVIRONMENTAL SAMPLES

Element	Qualitative	Quantitative	Unacceptable or unknown
Hydrogen			X
Helium			X
Neon			X
Argon			X
Krypton			X
Xenon			X
Oxygen			X
Carbon		X	
Nitrogen	X		
Bromine	X		
Iodine		X	
Boron		X	
Fluorine	X		
Phosphorus		X	
Sulfur		X	
Chlorine	X		

TABLE 4-80. DETECTION LIMITS FOR NOBLE METALS IN WATER BY ICP-AES AND DCP-AES (μg/L)

Element	ICP				DCP
	a	b	c	d	e
Ir	90	70	34	360	40
Pt	2	2	30	110	6
Au	0.9	0.9	10	70	2
Pd	6	6	2	30	6
Ru	90	60	2	90	20
Rh	6	3	1.5	30	30
Os	--	--	14	6	--

[a] Barnes (1978), simultaneous detection.

[b] Boumans (1979), simultaneous detection.

[c] Kirkbright and Tinsley (1979), simultaneous detection.

[d] Weymss and Scott (1978), sequential detection.

[e] Reednick (1979), simultaneous detection.

TABLE 4-81. QUANTITATION RANGE FOR NOBLE METALS IN AQUEOUS SOLUTION BY ICP-AES (EMSL-RTP 1982 PROTOCOL)

Element	Range (μg/L)
Au	6 to 5,000
Pt	50 to 5,000
Pd	90 to 5,000
Ru	1,200 to 10,000
Rh	580 to 5,000

Everett (1982) discussed problems with the direct determination of Pt, Pd, Rh, Ir, Ru, Au, Os, and Ag in precious metals industry process samples. Direct measurement was not possible due to high stray-light levels from high levels of Ca, Na, Zn, Ni, and Fe in these sample matrices. To permit their determination by ICP-AES, the precious metals were separated from acid digests of the matrix by precipitation with N, N-diphenylthiourea, and tin chloride. Osmium and silver were not recoverable quantitatively with this method or any others investigated. The other precious metals were determinable with 100-percent recoveries at 20 mg/L (5-percent RSD) and 1 mg/L (10-percent RSD). Detection limits in solution ranged from 0.1 to 0.5 mg/L.

Brown and Biggs (1984) investigated the determination of Pt and Pd in sulfide ores by using a simultaneous ICP-AES system. Pt and Pd must be separated from their base metals (other nonplatinum group metals present at high concentrations) to reduce the severe spectral interferences they cause. Fe (10 g/L), Ni (10 g/L), and Cu (10 g/L) completely swamp out the Pt emission line at 265.95 nm and the Pd emission line at 360.95 nm. These were the only two emission lines available on the direct reader they used. The Pt interference is due to a high spectral background while the Pd interference is due to a direct spectral overlap. Base metal separation is accomplished by a complicated sample digestion/ion-exchange procedure. The sample is digested in aqua regia on a hot plate and filtered. The residue and filter are digested in a mixture of $HF/HClO_4/HNO_3$, followed by another aqua regia digestion, another filtration, ashing, and fusion of the second filter and residue in a Zr crucible with sodium peroxide. The fusion mixture is dissolved in dilute HCl, combined with the filtrates from the two filtrations, and passed through a cation-exchange column to remove the base metals. Solution detection limits for Pt (50 mg/L) and Pd (40 mg/L) were defined as the concentrations of each element that gave a signal equal to twice the standard deviation of a series of 10 successive 10-s integrations of the blank solution. Analyses of Canadian Bureau of Mines CRMs were in agreement as were results obtained by other laboratories using classical fire-assay methods (Table 4-82). Laboratory comparisons of fire assay and ICP agreed within 5 percent for Pt and Pd for concentrations from

TABLE 4-82. DETERMINATION OF PLATINUM AND PALLADIUM IN SULFIDE ORE SAMPLES (μg/g) BY ICP-AES

Sample	Pt			Pd		
	Expected	Observed	Percent bias	Expected	Observed	Percent bias
Black sand ore	3.05	3.04	0			
Flotations sulfide concentrate	3.0	3.3	+10	12.7	13.1	+3
Ni-Cu concentrate	5.8	5.6	-3	8.1	8.1	0

50 to 300 μg/g. It is not clear whether the tedious sample preparation procedures could have been avoided if alternative analyte emission lines were available or if a sequential spectrometer were used instead of the simultaneous system.

Zamechek (1978) investigated the analysis of Pd, Pt, and Rh, in Si and Al metals and their oxides by ICP-AES. Both precision and detection limits and the lowest quantitatively determinable concentration (LQDC = 5 times the detection limit) were determined in aqueous solution and as a function of Al concentration (Table 4-83).

Brown and Luciano (1980) used a simultaneous ICP to determine precious metals in a series of amino-pyrite ore samples containing major concentrations of Fe and Cu and trace levels of Au. The Cu and Fe concentrations were more than 2 to 6 orders of magnitude greater than the Au concentration. Preparation of these samples for analysis of low levels of precious metals entails digesting the sample in a minimum total volume to ensure maximum analyte concentration and minimize sample dilution. This also increases total solids concentration, which can inhibit sample transport into the plasma. To evaluate the impact of solids concentration for these digested ores on precious metal determination, three types of nebulizers were evaluated (Table 4-84) with precision determinations based on 10 consecutive 10-s integrations of solutions containing 5 mg/L of each metal. The only precious metal found above detection limits in environmental samples was Au (0.025 to 15 mg/L in the digest). Fe was a significant spectral interference at concentrations >5,000 mg/L. The use of a simultaneous system facilitated correction on either side of the Au peak for Fe interference.

Ward et al. (1980) evaluated three techniques for biological and agricultural sample preparation using three commercially available simultaneous ICP spectrometers. Not all elements could be determined on the same spectrometer. However, all of the noble metals were prepared in the same calibration standard. None of the noble metals were found in any of the SRMs analyzed above the detection limits shown below.

Element	Detection limit (μg/g)
Ag	0.08
Au	0.1
Pt	0.8
Pd	1

Element	Detection limit (μg/g)
Rh	0.3
Ru	1.3
Ir	0.5
Os	1.3

TABLE 4-83. ICP-AES DETECTION LIMITS FOR Pd, Pt, AND Rh IN AQUEOUS SOLUTION

Element	LQDC	% RSD 1 mg/L	% RSD 0.1 mg/L
Pd	0.390	4	--
Pt	0.068	1	15
Rh	0.087	1	9

Source: Zamechek (1978)

TABLE 4-84. PRECISION DATA FOR PRECIOUS METALS ANALYSIS AS A FUNCTION OF SOLIDS CONTENT AND NEBULIZER TYPE

Analytical line (nm)	NaCl content			
	Blank	1%	5%	10%
Ag(328.0)				
AXF[a]	0.8	4	4	--
FXF[b]	0.6	2	3	3
HS[c]	0.9	0.7	0.6	2
Au(242.7)				
AXF	0.7	1	8	--
FXF	1	2	4	8
HS	1	1	1	1
Pt(203.6)				
AXF	0.5	1	7	--
FXF	0.8	3	2	6
HS	1	2	2	3
Pd(340.4)				
AXF	1	1	7	--
FXF	0.5	2	4	3
HS	0.4	0.5	1	1
Rh(343.4)				
AXF	1	1	8	--
FXF	0.8	1	1	5
HS	0.5	0.5	1	1
Ru(349.8)				
AXF	1	1	6	--
FXF	0.8	1	1	5
HS	1	0.5	0.7	1
Ir(224.2)				
AXF	0.6	1	8	--
FXF	0.4	2	3	5
HS	0.6	0.8	0.7	2
Os(225.6)				
AXF	0.8	3	6	--
FXF	0.8	1	3	6
HS	0.9	1	1	3

[a] AXF = Adjustable cross-flow nebulizer.

[b] FXF = Fixed cross-flow nebulizer.

[c] HS = High-solids nebulizer.

Available evidence suggests that ICP-AES can be used to determine all seven noble or precious metals (Table 4-85).

4.6.4 Determination of Volatile/Hydride-Forming Elements

4.6.4.1 Determination of Mercury--

Although mercury is a volatile element, it does not form a hydride and thus may be determined separately from the hydride formers, typically after generating a cold vapor from aqueous solution and measuring the response in the UV of appropriate absorption or emission lines. This effectively prevents the simultaneous or sequential determination of mercury with other elements in the same sample by ICP-AES, because direct-analysis detection limits are on the order of several hundred micrograms/liter and thus, some form of concentration such as the cold-vapor procedure must be used. Additional problems with the determination of mercury by ICP-AES are the possible extinction of the plasma during introduction of the vapor and changes in background emission, because nitrogen typically is used as a purge gas for mercury cold-vapor sample generation.

Suddendorf et al. (1981) have described an apparatus for determining mercury by ICP-AES. The basic modification from conventional cold-vapor generation systems is that the sample solution is injected into the reducing solution containing stannous chloride by a syringe through a rubber septum into a side arm of a completely sealed flask. The mercury vapor generated is then swept into the argon plasma by argon. Plasma extinction and background emission changes were not a problem. As many as 20 samples could be analyzed in succession without dismantling the equipment. The detection limit was 0.09 μg. The repeatability of the procedure was 1.4 percent at 0.66-μg injected mercury. The average mercury recovery from spiked halibut fish was 103 percent over the range 0.09- to 1.25-μg/g Hg (Table 4-86). Emission lines used for quantitation and any background correction were not identified.

It must be concluded that ICP-AES offers no clear advantage over cold-vapor atomic absorption for the determination of mercury even when a cold-vapor sample introduction is used.

TABLE 4-85. DOCUMENTED SINGLE ELEMENT COVERAGE CAPABILITY OF ICP-AES FOR NOBLE OR PRECIOUS METALS IN ENVIRONMENTAL SAMPLES

Element	Qualitative	Quantitative	Unacceptable or unknown
Gold		X	
Iridium		X	
Palladium		X	
Rhodium		X	
Ruthenium		X	
Silver		X	
Osmium		X	
Platinum		X	

TABLE 4-86. DETERMINATION OF MERCURY IN FISH BY ICP-AES

Mercury added (μg/g)	Mercury recovered (μg/g)	Percent recovery	RPD[a]
0.09	Not detectable	-	
0.09	Not detectable	-	
0.26	0.31	119	10
0.26	0.28	108	
0.65	0.68	105	3
0.65	0.66	102	
0.92	0.95	103	4
0.92	0.91	99	
1.25	1.28	102	2
1.25	1.26	101	

[a] RPD = Relative percent difference = $2\left|\frac{X_1 - X_2}{X_1 + X_2}\right| \times 100\%$.

4.6.4.2 Determination of Hydride-Forming Elements--

Because no examples of hydride generation interfacing with DCP-AES were found, this discussion will be restricted to ICP-AES applications. In considering the ICP-AES for comprehensive elemental analysis, there are significant problems associated with the detection and simultaneous quantification of germanium, arsenic, selenium, tin, antimony, tellurium, lead, and bismuth. These elements typically are present in environmental materials at very low levels; microgram or nanogram/kilogram in solids, and microgram or nanogram/liter in aqueous matrices. Conventional direct-sample nebulization into an ICP provides insufficient sensitivity to detect these elements. To overcome this problem, analysts have taken advantage of the well-known properties of these elements to form volatile hydrides after reduction with sodium borohydride, $NaBH_4$. The hydrides are generated either in a batch (pulsed) or a continuous flowing mode and are introduced into the plasma through an alternate argon stream (while the normal sample stream of argon is still flowing) or they are introduced directly through the nebulizer. Simultaneous multielement detection has been achieved for both batch and continuously generated hydrides by use of direct-reading polychromators. Some progress has been made in detection by sequential slew scanning monochromators, but this approach has not been studied extensively and is limited to continuous hydride-generation systems. No one has reported success in generating and detecting all of the above-named elements by ICP-AES on the same sample. Germanium, tin, lead, and tellurium appear to be the most intractable at present. Because they are priority pollutants and are on virtually every EPA list of concern, arsenic, antimony, and selenium have received the greatest attention in the development and application of the ICP-AES hydride interface.

The conclusion reached after study of available literature on ICP hydride generation is that there is no practical commercially available or homemade system that has been demonstrated to:

- Generate simultaneously all of the hydride forms of the elements interference-free.
- Interface adequately with a sequential spectrometer. This is a prerequisite for a goal of "near" simultaneous comprehensive multielement detection. Although several examples

of successful interfaces with simultaneous spectrometers are documented, polychromators do not meet the criterion of providing comprehensive capability.

The ICP-hydride interface is promising enough to warrant continued efforts to develop a continuously flowing generation system that generates stable interference-free hydrides of As, Se, Sb, Pb, Te, Bi, Sn, and Ge and will be suitable for interfacing with the nebulizer system of a sequential slew scanning monochromator; e.g., that of Eckhoff et al. (1982). The hydride-forming elements would be determined using a separate aliquot of sample. All other elements would then be determined after disconnection of the interface. This procedure is still not as simultaneous as SSMS, because a separate aliquot is necessary for hydride generation. The greatest advantage of this approach over current Level-1 SSMS is the improvement in detection limits from 0.1 mg/g to 0 to .01 μg/g in solids and from 1 mg/L to 1 ng/L in liquids. Simultaneous analysis of impinger solutions for As and Sb would also be achievable, reducing the number of analyses by a factor of 2, because AAS is the method currently called for in Level-1 SASS impinger analyses.

Specific applications of hydride generation to the determination of elements by ICP-AES follow.

The interfacing of hydride-generation techniques to ICP-AES systems has followed two courses: single-element determination, identical to the approach used in AAS, and multielement detection.

Single-element determination of arsenic by hydride reduction and ICP-AES detection was described by Fry et al. (1979), Broekaert and Liers (1980), and Pickford (1981), all using monochromator detection systems. Pickford's approach to sample introduction was novel in that batch samples were introduced through the nebulizer via a syringe technique and not through an alternate argon gas stream. Ikeda et al. (1981) used hydride ICP-AES with a polychromator to determine lead. Workman and Soltanpour (1980) used hydride ICP-AES with a polychromator to determine selenium in soils. Fry et al. (1979) also investigated several aspects of the hydride-generation and -collection process that are significant to simultaneous determination of elements. Batch preconcentration of the generated hydrides by trapping with liquid argon was shown to be an alternative to continuously flowing or batch-injection systems. Chemical reaction by products of hydride generation (H_2, H_2O, CO_2) that can extinguish the plasma or interfere with the detection process were investigated.

The simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium, and tellurium in aqueous solution by introduction into an ICP-AES was first demonstrated by Thompson et al. (1978a and b), using a continuously flowing hydride-generation system and a polychromator detection system. They later applied this technique to the analysis of these elements in water (Thompson et al. 1981), in soil and geological materials (Pahlavanpour et al. 1979, 1980), and to tin and germanium (Thompson and Pahlavanpour 1979). Because of numerous interferences, tin and germanium were found to be difficult to determine by this method. Detection limits on the order of 1 mg/L were achieved and were comparable to those reported for hydride analyses by AAS. They were more than 10 times lower than those obtained by conventional pneumatic nebulization into an ICP-AES. Ikeda et al. (1981) determined Pb, As, Sb, Bi, Sn, Te, and Se individually.

Ward et al. (1980) used a homemade hydride-generation system of the continuous-flow design to determine arsenic, antimony, selenium, tin, bismuth, and germanium in a variety of NBS biological SRMs as part of a larger study involving the evaluation of agricultural sample preparation techniques. Not all elements could be determined using the same ICP polychromator system due to unavailability of appropriate lines. As a result, at least two systems were required to determine all seven elements.

Wolnik et al. (1981) and Kahn et al. (1982) also coupled a hydride-generation system to an ICP-AES with a polychromator to determine As, Bi, Sb, Se, Te, and Sn in foods. The latter work employed a batch liquid argon condensation system to achieve lower detection limits and eliminate the interfering reaction byproducts noted by Fry et al. (1979). Even with cryogenic trapping, CO_2 still entered the plasma creating broad, transient signals that required background correction. Using NaOH to remove CO_2 was ruled out, because this would prohibit determination of Ge, Sn, and Se. Tellurium and lead were not detectable by this procedure.

Using a continuously flowing hydride-generation system and an ICP-AES polychromator detection system, Nygaard and Lowry (1982) evaluated sample-digestion procedures for simultaneous determination of As, Sb, and Se. Persulfate digestion of water samples in HNO_3 followed by heating at 95 °C in 6-M HCl was found to be the preferred method of digestion and compared favorably with the graphite-furnace AAS methods in EPA's Methods and Procedures Manual for Sampling and Analysis (1979).

Eckhoff et al. (1982) described a method in which hydrides of Ge, As, and Sb were chromatographically separated on Chromosorb 102 prior to determination by ICP-AES with a slew-scanning monochromator. They noted a potentially significant problem in using a scanning monochromator to detect hydride-generated elements. In batch generation systems, the hydrides appear as a pulse or slug and are available for analysis by the ICP-AES for only a short time. Thus, unless a polychromator is used, there will not be time to look at more than a single wavelength or a single element. The situation is not quite as clear with continuously generated hydrides. Factors such as integration time, sample concentration, and the time it takes for the monochromator grating to traverse or slew to the desired wavelengths are all significant in determining how many elements can be detected and at what concentration.

Stieg and Dennis (1982) have described an attachment that permits hydride introduction through the nebulizer rather than directly into the sample flow of argon, as most others have done. Using a continuous-flow system with direct introduction into the sample argon-plasma flow by means of an external-injection argon flow requires torch shutdown and reassembly when new samples are to be introduced through the nebulizer. This is a time-consuming process incompatible with routine multielemental screening. A detachable interface avoids this delay. This work was limited to the determination of As and Se by reduction with Al, and it will be left to others to confirm the utility of this approach to routine simultaneous analysis of t[illegible]ide elements.

Results [illegible] specific applications of ICP-AES with the hydride interface are given in Section 6.8. In general, it appears possible to determine all of the hydride-forming elements and mercury by ICP-AES although not optimally in the same sample (Table 4-87).

TABLE 4-87. DOCUMENTED SINGLE ELEMENT COVERAGE CAPABILITY FOR VOLATILE/HYDRIDE FORMING ELEMENTS IN ENVIRONMENTAL SAMPLES

Element	Qualitative	Quantitative	Unacceptable or unknown
Bismuth		X	
Mercury		X	
Arsenic		X	
Selenium		X	
Antimony		X	
Tin		X	
Osmium[a]			X
Lead[a]			X
Tellurium		X	
Germanium		X	

[a] Can be determined by conventional pneumatic nebulization.

4.6.5 Determination of Rare Earths and Lanthanides

The determination of rare earth elements (REE's) in environmental samples by ICP-AES has been limited to geological matrices, primarily because rock samples have been the only matrix of interest for analysts interested in rare earths. All studies agree that there are significant spectral interferences due to other elements that will require a cation separation of the final sample digestate. In most cases the sample must be fused either with lithium metaborate or sodium tetraborate to release the rare earths from the silicate matrix. The necessity of the cation exchange will preclude in all cases the inclusion of REE's in a simultaneous or sequential determination using a single sample. These sample preparation steps are not straightforward and are very time consuming.

Broekaert et al. (1979a) found that the high concentrations of sodium tetraborate used as a flux material to decompose rare earth minerals lowered the excitation temperature of the ICP plasma, thus decreasing the relative intensities of REE emission lines.

Broekaert et al. (1979b) reported detection limits of 0.1 to 30 mg/L for rare earth standards dissolved in HCl after fusion with $Na_2B_4O_7$ while Nikdel et al. (1979), using ICP-AES, determined detection limits of aqueous solutions of REE's in single-element solutions and in a mixture containing all REE's. The detection limit was defined as that concentration equivalent to a signal equal to three times that of the standard deviation of 16 consecutive 10-s integrations of the blank solution (Table 4-88). Walsh et al. (1981) used a conventional rock-dissolution procedure followed by a cation separation. The choice of spectral line was evaluated. Terbium and thulium could not be determined.

Crock and Lichte (1982) determined REE's in geological materials using a 63-channel simultaneous ICP-AES equipped with a modified Babington nebulizer. Thirty-second integration times were used for each element. Cadmium was added as an internal standard following sample preparation. Sample uptake was at 0.70 mL/min. Rock samples were prepared by a low-temperature multiacid digestion using hydrofluoric, nitric, and perchloric acids. If the REE's are suspected to be present in acid-resistant mineral form, a lithium metaborate fusion is used. In either case, after sample dissolution,

TABLE 4-88. DETECTION LIMITS FOR RARE EARTH ELEMENTS IN SINGLE-ELEMENT AND MULTIELEMENT MIXTURE, μg/L

Element	Wavelength, nm	Detection limit	
		Single	Mixture
La	394.91	5	5
Ce	394.27	20	10
Pr	391.89	20	20
Nd	401.22	10	10
Sm	360.95	20	20
Eu	420.50	3	4
Gd	376.84	10	7
Tb	350.92	9	10
Dy	353.17	8	7
Ho	345.6	8	7
Er	349.91	10	10
Tm	384.80	6	7
Yb	369.42	2	4
Lu	350.74	10	10

Source: Nikdel et al. (1979).

the remaining solution is evaporated to dryness, and the residue is dissolved in 50 mL of nitric acid and first passed through a cation exchange resin column, then an anion exchange column. The cation column removes Al, Be, Ca, Mn, Th, Ti, U, V, and Zr. The anion column removes Fe, which is present in the anion feed as a chloride. The anion column eluate is brought to 5 mL and analyzed by ICP-AES for REE's. The cation/anion separation procedure removes elements known to exhibit spectral interference with the REEs. Detection limits defined as twice the standard deviation of the background noise were consistent with those published for aqueous solutions (Table 4-89). Detection limits also were determined for an original 1-g sample diluted to a 5-mL final volume.

In general, all of the REE's can be determined by ICP-AES.

4.6.6 Determination of Alkali and Alkaline Earth Metals

All of the alkali and alkaline earth metals have been determined by ICP-AES. Table 4-90 summarizes some of this reported experience.

4.6.7 Determination of Transition Metals

All of the transition metals have been determined by ICP-AES. Table 4-90 summarizes some of this experience.

4.7 DATA QUALITY

4.7.1 Detection Limit

4.7.1.1 Volatile/Hydride-Forming Elements--

Detection limits for hydride-forming elements typically are based on three times the signal for a blank analyzed several times.

The data in Table 4-91 suggest several conclusions concerning the impact of hydride generation on element detection limits. First, regardless of the type of hydride generation/introduction system employed, detection limits are always 20 to 100 times lower than those obtained using conventional pneumatic nebulization. The batch concentration system of Kahn et al. (1982) gives the lowest detection limits, but obviously is more time consuming. In general, continuous-flow ICP/hydride systems appear capable of providing detection limits of 1 µg/L for arsenic, antimony, bismuth, selenium, and tellurium. Data for germanium, osmium, lead, and tin are insufficient to assess the state-of-the-art capability.

TABLE 4-89. REE WAVELENGTHS AND DETECTION LIMITS (IN SOLUTION)

	Wavelength, nm	Detection limit, μg/L	
		Published	Present study
La	398.8	11	4.3
Ce	418.7	52	31
Pr	422.2	47	64
Nd	430.3	75	22
Sm	442.2	54	30
Eu	381.9	2.7	0.9
Gd	303.2	27	18
Tb	367.6	60	58
Dy	340.7	27	25
Ho	345.6	5.7	3.6
Er	369.2	18	8.0
Tm	313.1	5.2	5.1
Yb	328.9	1.8	2.2
Lu	261.5	1.0	1.0
Y	321.6	7.9	1.8

Source: Crock and Lichte (1982)

TABLE 4-90. ELEMENTAL COVERAGE BY ICP-AES

Elements	Matrix	Conditions	Reference
Sn, Se; Hg, Cu, Cd, Pb; U; Ni, Bi, Te	Urine	Resin preconcentration; sequential determination	Barnes and Genna 1979
Cu, Fe; Co, Ni; Mo, Ti, V; Pb, U, Th; Ce, La; Mn, Zn	Fuel oil, shale oil, coal	Same	Mahanti and Barnes, 1983a
Cu, Fe, Si, Ti, V; Al	Graphite	Same	Mahanti and Barnes 1983b
Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, Zn	Coal, coal fly ash	Various ashing, bomb combustion and fusion procedures; simultaneous determination	McGrath 1984
Al, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, V, Zn	Fly ash	Same as above	Nadharni 1980
As, B, Pb	Coal, orchard leaves, shale oil	Oxygen bomb, dissolution	Nadkarni 1981
Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Ag, Na, Sr, Th, Sn, Ti, V, Zn	Coal, hopper ash	Acid bomb dissolution	Shendrikar 1980
As, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Mo, Pi, Pb, Sr, Zn; Al, Cd, Cu, Fe, Mg, Mn, P, Pb, Zn, K	Air particulates, water samples, soil samples	Acid digestions	McQuaker et al. 1979

(continued)

TABLE 4-90 (continued)

Elements	Matrix	Conditions	Reference
Al, Fe, Ca, K, Mg, Ti, Mn, Ba, Sr, Zn, Pb, Ag, Sb, Cd	Air particulates, soil	Acid digestions	Lynch et al. 1980
Al, B, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, Zn	Coal fly ash, air particulates	Acid digestions	Hee et al. 1982
Ge	Coal, coal fly ash	Dry and wet ashing	Nadkarni and Botto 1984
Ba, Co, Cr, Cu, Li, Ni, Sc, Sr, V, Zr	Silicate rocks	Acid dissolution	Uchida et al. 1980
Na, Mg, Ca, Al, Cr, Ti, V, Mn, Fe, Co, Cu, Zn, Ba; Al, Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, Sr	Air particulates, pine needles	Low temperature ashing, acid dissolution	Fogg and Seeley 1984
Ag, Au, Bi, Cd, Cu, Pb, Zn	MIBK, water, soil	Acid digestion, extraction	Motooka et al. 1979
Cr, Fe, Mn, Ti, Zn, Ba, Co, Cu, V, Ca, Ni	Cement, coal fly ash, coal river sediment	Acid bomb dissolution	Branscome et al. 1985
Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, Zr	Peanuts, wheat, spinach	Acid bomb dissolution	Kuennen et al. 1982
Si, Al, Fe, Ti, Mn, Ca, Mg, Na, K	Silicate rocks	Acid dissolution	Uchida et al. 1979

(continued)

TABLE 4-90 (continued)

Elements	Matrix	Conditions	Reference
Si, Al, Ti, Ca, Mg, Na, Fe, Mn, Cr, Ba, Zr, Cu	Silicate rocks	Metaborate fusion	Burman et al. 1978
Se, Al, Fe, Mg, Ca, Na, K, Ti, Mn, P	Silicate rocks	Fusion	Walsh 1980
Al, Ca, Fe, Mg, Ti, As, In, La, Ba, Be, Ce, Co, Cr, Cu, Eu, Ga, La, Mn, Ni, Pb, Pr, Sc, Sr, V, Y, Yb, Zn, Zr, Cd, Se, Dy, Er, Gd, Hf, Ir, Lu, Nb, Nd, Th	Coal, coal fly ash, river sediment, urban particulate matter, silicate rocks	Fusion, acid dissolution	Floyd et al. 1982
Ba, Be, Fe, Mn, Mo, Sr, V, Cd, Cr, Co, Cu, Ni, Zn, Ag, Ca, K, Mg, Na, Th, Al, Na, P, Ti	Water, soil	Acid digestion	Gaskill 1982
Mo, Co, B	Soil extracts	Extraction	Mazoori 1982
P, K, Zn, Fe, Ca, Mn	Soil extracts	Extraction	Soltanpour 1979
Si, Al, Fe, Ca, Mg, Na, K, Mn, Ti, P, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sr, Th, V, Zn, Y	Soil	Acid bomb dissolution	Lechler et al. 1980
B, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Zn	Sewage sludge	Acid digestion	Mosely and Vijan 1981

(continued)

TABLE 4-90 (continued)

Elements	Matrix	Conditions	Reference
Fe, Al, Ca, Zn, Cd, Co, Mg, Mn, Cr, Cu, Ni, Pb, Mo, Sr, Ti	Sewage sludge	Acid digestion	Clevenger et al. 1983
Ca, Cu, Zn	Animal feed	Acid digestion	Blakemore and Billedeau 1981
Mg, Fe, Zn	Fertilizer	Acid digestion	Aten et al. 1983
B, Ca, Cu, Fe, Mg, Mn, P, K, Zn	Fertilizer	Acid digestion	Jones 1982

TABLE 4-91. DETECTION LIMITS OBTAINED USING VARIOUS HYDRIDE GENERATION SYSTEMS INTERFACED WITH ICP-AES (μg/L)

Element	Batch[a]	Tandem nebulization[b]	Continuous flow[c]	d	Sequential[e]	Conventional pneumatic nebulization[b]
Arsenic	0.02	3	0.8	1	1	20
Antimony	0.08	0.7	1.0	3	5	20
Bismuth	0.3	0.9	0.8	--	2	40
Germanium	0.6	20	--	--	--	200
Lead	--	--	--	--	1	30
Osmium	--	--	--	--	--	--
Selenium	0.1	0.5	0.8	1	1	20
Tellurium	--	0.7	1.0	--	2	20
Tin	0.8	--	--	--	0.5	100

[a] Kahn et al. (1982), hydride generation/condensation.

[b] Wolnik et al. (1981)

[c] Thompson et al. (1978)

[d] Nygaard and Lowry (1982)

[e] Ikeda et al. (1981)

4.7.1.2 Noble or Precious Metals--

See Table 4-80.

4.7.1.3 Rare Earths and Lanthanides--

Detection limits for rare earth and lanthanide elements as discussed in Section 4.6.5 are given in Tables 4-88, 4-89, and 4-92.

4.7.1.4 Alkali/Alkaline Earths--

See Table 4-57.

4.7.1.5 Transition Metals--

See Table 4-57.

4.7.2 Precision

4.7.2.1 Volatile/Hydride-Forming Elements--

Precision data for hydride-forming elements are given in Table 4-93 and have been summarized in Table 4-94 according to matrix type and concentration range. Precisions for most elements for which data were available were less than 20-percent RSD. As expected, the best precision was achieved for a clean water matrix.

4.7.2.2 Noble or Precious Metals--

Data presented in Section 4.3 indicate that precisions on the order of 20-percent RSD or better can be expected for samples requiring preparation.

4.7.2.3 Rare Earths and Lanthanides--

Precision data for REE's in standard soil, rock, and coal samples are given in Tables 4-95, 4-96, and 4-97. In all cases, reported values are based on the mean and 95-percent confidence limits of four replicate sample preparations.

4.7.2.4 Alkali/Alkaline Earth Metals--

Data presented in Section 4.3 indicate that precisions on the order of 20-percent RSD or better can be expected for samples requiring preparation.

4.7.3 Accuracy

4.7.3.1 Volatile/Hydride-Forming Elements--

Recovery data for hydride-forming elements given in Table 4-98 have been summarized in Table 4-99 according to matrix type and concentration

TABLE 4-92. DETECTION LIMITS IN SAMPLE BY ICP/AES[a]

Element	Chondrite normalizing value	Detection limits for 1 g sample diluted to a 5-mL final volume
La	0.330	0.022
Ce	0.88	0.155
Pr	0.11	0.32
Nd	0.60	0.11
Sm	0.181	0.15
Eu	0.069	0.0045
Gd	0.249	0.090
Tb	0.047	0.29
Dy	0.325	0.125
Ho	0.070	0.018
Er	0.200	0.040
Tm	0.030	0.026
Yb	0.200	0.011
Lu	0.034	0.005
Y	1.96	0.009

[a] All values are μg/g.

Source: Crock and Lichte (1982)

TABLE 4-93. PRECISION OF ICP-AES FOR ELEMENTS INTRODUCED BY HYDRIDE GENERATION

Element	Matrix	Measured concentration	% RSD
Arsenic	Water (deionized)	1 µg/L[a] 10 µg/L[a] 29 µg/L[b] 93 µg/L[b]	3 2 0 1
	Soil 04 (CANMET Standard)	6.45 µg/g[c]	1
	Orchard Leaves (NBS-SRM 1571)	10 µg/g[d] 13 µg/g[a] 10.2 µg/g[e]	20 8 6
	Rice flour (NBS-SRM 1568)	0.452 µg/g[f] 0.44 µg/g[a] 0.40 µg/g[e]	15 11 5
	Wheat flour (NBS-SRM 1567)	0.006 µg/g[a]	17
	Spinach (NBS-SRM 1570)	0.17 µg/g[a] 0.15 µg/g[e]	6 17
	Pine needles (NBS-SRM 1575)	0.21 µg/g[e]	10
	Tomato leaves (NBS-SRM 1573)	0.26 µg/g[e]	5
	Pepperbush (N.I.E.S. #1)	1.1 µg/g[e]	4
	Bovine liver (NBS-SRM 1577)	0.05 µg/g[e]	34
Antimony	Water (deionized)	0.8 µg/L[a] 10 µg/L[a]	2 2
	Soil 04	0.25 µg/g[c]	12
	Orchard leaves (NBS-SRM 1571)	2.8 µg/g[a] 2.9 µg/g[d] 2.5 µg/g[e]	4 10 7

See footnotes at end of table.

(continued)

TABLE 4-93 (continued)

Element	Matrix	Measured concentration	% RSD
Antimony (continued)	Pine needles (NBS-SRM 1575)	0.20 μg/g[e]	11
	Pepperbush (N.I.E.S. #1)	0.8 μg/g[e]	5
	Spinach (NBS-SRM 1570)	0.014 μg/g[a]	21
Bismuth	Water (deionized)	2 μg/L[a] 10 μg/L[a]	2 4
	Soil 04	0.19 μg/g[c]	11
	Orchard leaves (NBS-SRM 1571)	0.06 μg/g[e]	14
	Pine needles (NBS-SRM 1575)	0.45 μg/g[e]	14
	Spinach (NBS-SRM 1570)	1.5 μg/g[e]	6
	Tomato leaves (NBS-SRM 1573)	1.0 μg/g[e]	17
	Pepperbush (N.I.E.S. #1)	0.60 μg/g[e]	4
Germanium	Water (deionized)	4 μg/L[a] 10 μg/L[a]	8 6
	Water (EPA standard)	50 μg/L[b] 100 μg/L[b]	1 2
	Orchard leaves (NBS-SRM 1571)	0.12 μg/g	35
	Wheat flour (NBS-SRM 1567)	0.12 μg/g	35
Lead		NO DATA AVAILABLE	
Osmium		NO DATA AVAILABLE	

See footnotes at end of table.

(continued)

TABLE 4-93 (continued)

Element	Matrix	Measured concentration	% RSD
Selenium	Water (deionized)	2 μg/L[a]	9
		10 μg/L[a]	4
	Rice flour (NBS-SRM 1568	0.37 μg/g[a]	17
		0.33 μg/g[f]	9
		0.11 μg/g[e]	19
	Wheat flour (NBS-SRM 1567	0.19 μg/g[e]	13
		0.87 μg/g[a]	7
	Orchard leaves (NBS-SRM 1571)	0.07 μg/g[a]	14
		0.08 μg/g[e]	21
	Bovine liver (NBS-SRM 1577)	0.8 μg/g[e]	5
	Pine needles (NBS-SRM 1575)	0.09 μg/g[e]	14
	Pepperbush (N.I.E.S. #1)	0.11 μg/g[e]	19
Tellurium	Water (deionized)	4 μg/L[a]	6
		10 μg/L[a]	5
	Orchard leaves (NBS-SRM 1571)	0.18 μg/g[a]	6
		0.19 μg/g[e]	33
	Pepperbush (N.I.E.S. #1)	0.17 μg/g[e]	37
Tin	Orchard leaves (NBS-SRM 1571)	0.19 μg/g[e]	34
	Pepperbush (N.I.E.S. #1)	0.17 μg/g[e]	37

[a] Kahn et al. (1982)
[b] Eckoff et al. (1982)
[c] Pahlavanpour et al. (1980)
[d] Pahlavanpour et al. (1979)
[e] Ward et al. (1980)
[f] Wolnik et al. (1981)

TABLE 4-94. SUMMARY OF PRECISION DATA FOR ICP-AES WITH HYDRIDE GENERATION

Element	Matrix	Concentration range	% RSD
Arsenic	Clean water	1-100 µg/L	1-4
	Soil	6.5 µg/g	1
	Plant materials	0.01-10 µg/g	4-20
	Liver	0.05 µg/g	34
Antimony	Clean water	1-25 µg/L	1-4
	Soil	0.25 µg/g	12
	Plant materials	0.01-3 µg/g	4-20
Bismuth	Clean water	2-10 µg/L	2-4
	Soil	0.19 µg/g	11
	Plant materials	0.06-1.5 µg/g	4-17
Germanium	Clean water	5-100 µg/L	1-8
	Plant materials	0.12 µg/g	35
Lead	NO DATA AVAILABLE		
Osmium	NO DATA AVAILABLE		
Selenium	Clean water	2-25 µg/L	1-9
	Plant materials	0.1-1.0 µg/g	9-21
	Liver	0.8 µg/g	5
	Clean water	4-10 µg/L	5
Tellurium	Plant materials	0.18 µg/g	33-37

TABLE 4-95. NBS SRM 1632a COAL[a]
(μg/g)

Element	Expected	Observed	Percent bias	% RSD
Ce	29	28.5 ± 0.4	-2	1
Dy	2.2	2.1 ± 0.1	-5	5
Er	--	0.91 ± 0.05	--	5
En	0.550	0.49 ± 0.01	-11	2
Gd	1.95	2.4 ± 0.2	+23	8
Ho	--	0.38 ± 0.05	--	13
La	16	14.5 ± 0.2	-9	1
Lu	0.200	0.15 ± 0.01	-25	7
Nd	12.0	13.0 ± 0.1	+8	1
Pr	--	3.3 ± 0.1	--	3
Sm	2.3	2.6 ± 0.1	+13	4
Tb	0.340	0.3 ± 0.1	-12	33
Tm	--	0.4 ± 0.1	--	25
Y	--	8.3 ± 0.5	--	6
Yb	1.1	0.90 ± 0.01	-18	1

[a] Ashed overnight at 525 °C and then subjected to acid dissolution cation separation.

Source: Crock and Lichte (1982)

TABLE 4-96. CANADIAN SO-2 SOIL

Element	Expected	Observed	Percent bias	% RSD
Ce	112 ± 17	111 ± 3	-1	3
Dy	11	8.6 ± 0.1	-21	1
Er	4.8	4.1 ± 0.1	-15	2
Eu	3.7 ± 0.6	3.43 ± 0.02	-7	1
Gd	11	10.3 ± 0.2	-6	2
Ho	2	1.71 ± 0.05	-14	3
La	48 ± 2	46 ± 1	-4	2
Lu	0.5	0.47 ± 0.04	-18	9
Nd	57	57 ± 1	0	2
Pr	15	13.4 ± 0.4	-11	3
Sm	12 ± 2	12.2 ± 0.1	+2	8
Tb	1.8	1.3 ± 0.2	-28	15
Tm	0.8	0.54 ± 0.02	-32	4
Y	40 ± 5	37.2 ± 0.5	-7	1
Yb	4	3.39 ± 0.01	-15	0

Acid digestion.

Source: Crock and Lichte (1982)

TABLE 4-97. USGS STANDARD BASALT BCR-1[a]
(μg/g)

Element	Expected	Observed	Percent bias	% RSD
Y	40	35.3 ± 0.3	-12	1
La	27	26.6 ± 0.2	-3	1
Ce	53	53.8 ± 0.2	+2	0
Pr	7	7.29 ± 0.06	+4	0
Nd	26	29.7 ± 0.3	+14	1
Sm	6.5	6.7 ± 0.3	+3	4
Eu	2.0	1.98 ± 0.08	-1	4
Gd	6.6	6.9 ± 0.2	+5	3
Tb	1.0	1.0 ± 0.1	0	10
Dy	7	6.72 ± 0.08	-4	1
Ho	1.2	1.40 ± 0.02	+17	1
Er	3.5	3.80 ± 0.03	+9	1
Tm	0.6	0.57 ± 0.02	-5	4
Yb	3.4	3.70 ± 0.03	+9	1
Lu	0.5	0.524 ± 0.004	+5	1

[a] Prepared by lithium metaborate fusion.

TABLE 4-98. ACCURACY OF ICAP-AES FOR ELEMENTS INTRODUCED BY HYDRIDE GENERATION

Element	Matrix	Measured concentration	Expected concentration	% Recovery
Arsenic	Water (EPA QC)	60 μg/L[a]	61 μg/L	98
	Water (NBS-SRM 1643)	71 μg/L[a]	76 μg/L	93
	Bituminous coal effluent spike	104 μg/L[a]	100 μg/L	104
	Electric services effluent spike	103 μg/L[a]	100 μg/L	103
	Sewage treatment plant effluent spike	104 μg/L[a]	100 μg/L	104
	Petroleum refining effluent spike	104 μg/L[a]	100 μg/L	104
	Fabricated rubber products effluent spike	104 μg/L[a]	100 μg/L	104
	Blast furnace effluent spike	105 μg/L[a]	100 μg/L	105
	Ferroalloy ore effluent spike	101 μg/L[a]	100 μg/L	101
	Paper mill effluent spike	104 μg/L[a]	100 μg/L	104
	Zinc smelting effluent spike	101 μg/L[a]	100 μg/L	101
	Industrial inorganic chemicals effluent spike	105 μg/L[a]	100 μg/L	105
	River sediment[b] (NBS-SRM 1645)	67 μg/L[a]	66 μg/L	102
	Coal fly ash[b] (NBS-SRM 1633)	57 μg/L[a]	61 μg/L	93

See footnotes at end of table.

(continued)

TABLE 4-98 (continued)

Element	Matrix	Measured concentration	Expected concentration	% Recovery
Arsenic (continued)	Urban particulate matter[b] (NBS-SRM 1648)	117 μg/L[a]	115 μg/L	102
	Water (EPA QC)	29 μg/L[c]	22 μg/L	132
		92 μg/L[c]	98 μg/L	94
	Soil (Canadian certified) (Materials project) (Standard soils)			
	SO-1	1.94 μg/g[d]	1.9 μg/g	102
	SO-2	0.77 μg/g[d]	1.2 μg/g	64
	SO-3	2.32 μg/g[d]	2.6 μg/g	89
	SO-4	6.45 μg/g[d]	7.1 μg/g	91
	Orchard leaves (NBS-SRM 1571)	10.2 μg/g[e]	10 μg/g	102
		9.7 μg/g[e]	10 μg/g	97
		9.5 μg/g[e]	10 μg/g	95
		10 μg/g[f]	11.98 μg/g	83
		13 μg/g[g]	14 μg/g	93
		10.2 μg/g[h]	10 μg/g	102
	Rice flour (NBS-SRM 1568)	0.44 μg/g[g]	0.41 μg/g	107
		0.452 μg/g[i]	0.41 μg/g	110
		0.40 μg/g[h]	0.41 μg/g	98
	Spiked	0.10 μg/g[g]	--	99-104
		0.25 μg/g[g]	--	99-103
		1.0 μg/g[i]	--	112
		0.25 μg/g[i]	--	50
	Wheat flour (NBS-SRM 1567)	0.006 μg/g[g]	0.006 μg/g	100
	Spiked	1.0 μg/g[i]	--	115
	Spinach (NBS-SRM 1570)	0.17 μg/g[g]	0.15 μg/g	113
		0.15 μg/g[h]	0.15 μg/g	100
	Tomato leaves (NBS-SRM 1573)	0.29 μg/g[e]	0.27 μg/g	107
		0.25 μg/g[e]	0.27 μg/g	93
		0.26 μg/g[h]	0.27 μg/g	96

tnotes at end of table. (continued)

TABLE 4-98 (continued)

Element	Matrix	Measured concentration	Expected concentration	% Recovery
Arsenic (continued)	Pine needles (NBS-SRM 1575)	0.21 μg/g[h]	0.21 μg/g	100
	Pepperbush (N.I.E.S. #1)	1.1 μg/g[h]	3 μg/g	37
	Bowen's kale	0.14 μg/g[f]	0.268 μg/g	52
	Liver (NBS-SRM 1577)	0.05 μg/g[h]	0.055 μg/g	91
Antimony	Water (EPA QC)	9 μg/L[a]	8 μg/L	113
	Bituminous coal effluent spike	104 μg/L[a]	100 μg/L	104
	Electric services effluent spike	103 μg/L[a]	100 μg/L	103
	Sewage treatment plant effluent spike	104 μg/L[a]	100 μg/L	104
	Petroleum refining effluent spike	103 μg/L[a]	100 μg/L	103
	Fabricated rubber products effluent spike	99 μg/L[a]	100 μg/L	99
	Blast furnace effluent spike	104 μg/L[a]	100 μg/L	104
	Ferroalloy ore effluent spike	99 μg/L[a]	100 μg/L	99
	Paper mill Effluent spike	103 μg/L[a]	100 μg/L	103
	Zinc smelting effluent spike	99 μg/L[a]	100 μg/L	99
	Industrial inorganic chemicals effluent spike	109 μg/L[a]	100 μg/L	109

See footnotes at end of table.

(continued)

TABLE 4-98 (continued)

Element	Matrix	Measured concentration	Expected concentration	% Recovery
Antimony (continued)	River sediment[b] (NBS-SRM 1645)	38 μg/L[a]	51 μg/L	75
	Coal fly ash[b] (NBS-SRM 1633)	5 μg/L[a]	8 μg/L	63
	Urban particulate[b] matter	41 μg/L[a]	45 μg/L	91
	Soil (Canadian certified materials project standard soils)			
	SO-1	0.12 μg/g[d]	0.2	60
	SO-2	0.1 μg/g[d]	0.1	100
	SO-3	0.22 μg/g[d]	0.3	73
	SO-4	0.25 μg/g[d]	0.7	36
	Orchard leaves (NBS-SRM 1571)	2.8 μg/g[g]	2.9 μg/g	97
		2.5 μg/g[h]	2.9 μg/g	86
		2.9 μg/g[f]	2.77 μg/g	105
	Rice flour (NBS-SRM 1568) amount spiked	0.10 μg/g[g]		80-95
		0.25 μg/g[g]		84-92
		0.50 μg/g[i]		47
		2.50 μg/g[i]		52
	Spinach (NBS-SRM 1570)	0.014 μg/g[g]	0.04 μg/g	35
	Pine needles (NBS-SRM 1575)	0.20 μg/g[h]	0.2 μg/g	100
	Pepperbush (N.I.E.S. #1)	0.8 μg/g[h]	2.5 μg/g	32
	Bowen's kale	0.070[f]	0.075	93

See footnotes at end of table.

(continued)

TABLE 4-98 (continued)

Element	Matrix	Measured concen-tration	Expected concen-tration	% Recovery
Bismuth	Soil (Canadian certified materials project standard soils)			
	SO-1	0.24[d]	0.5	48
	SO-2	0.03[d]	0.1	33
	SO-3	0.03[d]	0.1	33
	SO-4	0.19[d]	0.1	190
	Orchard leaves (NBS-SRM 1571)	0.06[h]	0.1	60
	Rice flour (NBS-SRM 1568) amount spiked	0.25 µg/g[i]	--	96
		0.10 µg/g[g]	--	97
		0.25 µg/g[g]	--	87-90
		1.0 µg/g[i]	--	115
	Wheat flour (NBS-SRM 1567) amount spiked	1.0 µg/g[i]	--	115
Germanium	Water (EPA QC)	48.7 µg/L[c]	50 µg/L	97
		93 µg/L[c]	100 µg/L	93
	Rice flour (NBS-SRM) amount spiked	0.1 µg/g[g]		89-108
		0.25 µg/g		91-102
		10.0 µg/g[i]		114
	Wheat flour (NBS-SRM 1567) amount spiked	10.0 µg/g[i]		0
Lead		NO DATA AVAILABLE		
Osmium		NO DATA AVAILABLE		
Selenium	Water (EPA QC)	14 µg/L[a]	16 µg/L	88

See footnotes at end of table.

(continued)

TABLE 4-98 (continued)

Element	Matrix	Measured concentration	Expected concentration	% Recovery
Selenium (continued)	Water (NBS-SRM 1643)	10 µg/L[a]	12 µg/L	83
	Bituminous coal effluent spike	105 µg/L[a]	100 µg/L	105
	Electric services effluent spike	106 µg/L[a]	100 µg/L	106
	Sewage treatment plant effluent spike	106 µg/L[a]	100 µg/L	106
	Petroleum refining effluent spike	105 µg/L[a]	100 µg/L	105
	Fabricated rubber products effluent spike	104 µg/L[a]	100 µg/L	104
	Blast furnace effluent spike	105 µg/L[a]	100 µg/L	105
	Ferroalloy ores effluent spike	103 µg/L[a]	100 µg/L	103
	Paper mill effluent spike	103 µg/L[a]	100 µg/L	103
	Zinc smelting effluent spike	94 µg/L[a]	100 µg/L	94
	Industrial inorganic chemicals effluent spike	103 µg/L[a]	100 µg/L	103
	Coal fly ash[b] (NBS-SRM 1633)	9 µg/L[a]	9 µg/L	100
	Urban particulate[b] matter (NBS-SRM 1648)	26 µg/L[a]	24 µg/L	108
	Rice flour (NBS-SRM 1568)	0.11 µg/g[h] 0.33 µg/g[i] 0.37 µg/g[g]	0.4 µg/g 0.4 µg/g 0.4 µg/g	28 83 93

See footnotes at end of table.

(continued)

TABLE 4-98 (continued)

Element	Matrix	Measured concentration	Expected concentration	% Recovery
Selenium (continued)	Spiked	0.10 μg/g[g]	--	89-96
		0.25 μg/g[g]	--	97-101
		0.25 μg/g[i]	--	92
		1.00 μg/g[i]	--	96
	Wheat flour (NBS-SRM 1567)	0.19 μg/g[h]	1.1 μg/g	173
		0.831 μg/g[i]	1.1 μg/g	76
		0.909 μg/g[i]	1.1 μg/g	83
		0.87 μg/g[g]	1.1 μg/g	79
	Spiked	1.00 μg/g[i]	--	77
	Liver (NBS-SRM)	0.8 μg/g[h]	1.1 μg/g	73
	Orchard leaves (NBS-SRM 1571)	0.08 μg/g[h]	0.08 μg/g	100
		0.07 μg/g[g]	0.08 μg/g	88
Tellurium	Rice flour (NBS-SRM 1568) Spiked	0.25 μg/g[i]	--	105
		1.0 μg/g[i]	--	104
	Wheat flour (NBS-SRM 1567) Spiked	1.0 μg/g[i]	--	103
	Orchard leaves	0.5 μg/g[h]	0.01 μg/g	5,000
Tin	Rice flour (NBS-SRM 1568) Spiked	0.10 μg/g[g]		71-108
		0.25 μg/g		94-114

[a] Nygaard and Lowry (1982)

[b] Solids digested as 0.025 g in 25 mL water.

[c] Eckhoff et al. (1982)

[d] Pahlavanpour et al. (1980)

[e] Pickford (1981)

[f] Pahlavanpour et al. (1980)

[g] Kahn et al. (1982)

[h] Ward et al. (1981)

[i] Wolnik et al. (1981)

TABLE 4-99. SUMMARY OF ACCURACY DATA FOR ICP-AES WITH HYDRIDE GENERATION

Element	Matrix	Concentration range	% Recovery
Arsenic	Clean water	20-100 µg/L	93-132
	Effluent water	100 µg/L	101-105
	River sediment	66 µg/L	102
	Coal fly ash	61 µg/L	93
	Particulate matter	115 µg/L	102
	Soil	1-7 µg/g	64-102
	Plant materials	0.01-10 µg/g	37-115
	Liver	0.05 µg/g	91
Antimony	Clean water	8 µg/L	113
	Effluent water	100 µg/L	99-113
	River sediment	51 µg/L	75
	Coal fly ash	8 µg/L	63
	Particulate matter	45 µg/L	91
	Soil	0.1-0.3 µg/g	36-100
	Plant materials	0.05-3 µg/g	32-100
Bismuth	Soil	0.1-0.5 µg/g	33-190
	Plant materials	0.1-1.0 µg/g	60-115
Germanium	Clean water	50-100 µg/L	93-97
	Plant materials	0.1-10 µg/g	0-114
Lead	NO DATA AVAILABLE		
Osmium	NO DATA AVAILABLE		
Selenium	Clean water	12-16 µg/L	83-88
	Effluent water	100 µg/L	94-105
	Coal fly ash	9 µg/L	100
	Particulate matter	24 µg/L	108
	Plant materials	0.1-1.0 µg/g	28-173
	Liver	1.1 µg/g	73
Tellurium	Plant materials	0.25-1.0 µg/g	103-5,000
Tin	Plant materials	0.1-0.25 µg/g	71-114

range. Arsenic and selenium recoveries were generally 90 percent or better for all matrices except plant materials where, for several materials, low recoveries were reported. In general, arsenic and selenium recoveries from plant materials were also greater than 90 percent. Antimony recovery data were generally greater than 80 percent for all matrices except for soil and plant materials, which experienced lower recoveries. Data for bismuth, germanium, lead, osmium, tellurium, and tin either were not available or were available for only a limited number of matrices. Recovery data varied greatly and are probably inconclusive for these elements.

The ICP-AES precision, accuracy, and detection limit data for hydride-forming elements are summarized in Table 4-100. The data probably are conclusive only for arsenic, selenium, and antimony because of the small amount of data for other elements. This is probably because arsenic, selenium, and antimony are regulated elements of some concern whereas the rest generally are not. Lead and osmium are regulated, but have not been studied successfully using ICP-AES with the hydride interface.

4.7.3.2 Noble or Precious Metals--

Data presented in Section 4.3 indicate that accuracies on the order of ± 25 percent as percent bias can be expected for prepared samples.

4.7.3.3 Rare Earths and Lanthanides--

See data in Tables 4-101, 4-102, and 4-103.

4.7.3.4 Alkali/Alkaline Earth Metals--

Data presented in Section 4.3 indicate that accuracies on the order of ± 25 percent as percent bias can be expected for prepared samples.

4.7.3.5 Transition Metals--

Data presented in Section 4.3 indicate that accuracies on the order of ± 25 percent as percent bias can be expected for prepared samples.

4.8 STANDARD OPERATING PROCEDURES

Five protocols have been produced by EPA and ASTM for analysis of samples by ICP spectroscopy.

ASTM Committee D-19 (water) has proposed test methods for elements in water by ICP-AES. EMSL-RTP has developed a protocol for the ICP-AES analysis

TABLE 4-100. SUMMARY OF PRECISION, ACCURACY, AND DETECTION LIMIT DATA FOR ICP-AES WITH HYDRIDE GENERATION FOR ENVIRONMENTAL MATRICES[a]

Element	% RSD	% Recovery	Detection limit (μg/L)
Arsenic	1-34	93-132	0.02-3
Antimony	1-20	32-113	0.08-5
Bismuth	2-17	33-190	0.3-2
Germanium	1-35	0-114	0.6-20
Lead	--	--	1
Osmium	--	--	--
Selenium	1-21	28-173	0.1-1
Tellurium	5-37	103-5,000	0.7-2
Tin	34-37	71-114	0.5-0.8

[a] Generally detection limits have been determined for clean matrices only, typically deionized water.

TABLE 4-101. STANDARD BASALT BHVO-1[a] (μg/g)

Element	Expected	Observed	% Bias	% RSD
Y	28 ± 2	25.7 ± 0.3	-8	1
La	16.7 ± 0.8	16.2 ± 0.1	-3	1
Ce	41 ± 4	38.2 ± 0.7	-7	2
Pr	5.6	5.66 ± 0.05	1	1
Nd	24 ± 6	25.4 ± 0.2	+6	1
Sm	6.1 ± 0.7	6.4 ± 0.2	+5	3
Eu	2.0 ± 0.4	2.18 ± 0.07	+9	3
Gd	7 ± 2	7.0 ± 0.3	0	4
Tb	1.0 ± 0.2	0.86 ± 0.08	-14	9
Dy	4.8 ± 0.26	5.59 ± 0.07	+16	1
Ho	0.94	1.06 ± 0.04	+13	4
Er	2.0 ± 0.3	2.63 ± 0.03	+32	1
Tm	0.31 ± 0.04	0.34 ± 0.02	+10	6
Yb	2.1 ± 0.5	2.19 ± 0.03	+4	1
Lu	0.32	0.291 ± 0.003	-9	1

[a] Prepared by lithium metaborate fusion.

TABLE 4-102. USGS AGV-1 ANDESITE

Element	Lit. (24)	Found[a]	% Bias	Found[b]	% Bias
Ce	71	69 ± 1	-3	72 ± 2	+1
Dy	3.5	3.7 ± 0.05	+6	3.6 ± 0.1	+3
Er	1.2	1.8 ± 0.06	+50	2.0 ± 0.3	+67
Eu	1.6	1.6 ± 0.07	0	1.6 ± 0.05	0
Gd	5.5	4.6 ± 0.1	-16	4.5 ± 0.2	-18
Ho	0.6	0.70 ± .06	+17	0.6 ± 0.05	0
La	36	39 ± 1	+8	38 ± 2	+6
Lu	0.3	0.264 ± 0.002	-12	0.30 ± 0.03	0
Nd	37	32.0 ± 0.5	-14	31 ± 2	-16
Pr	7	8.5 ± 0.2	+21	9 ± 1	+29
Sm	5.9	5.8 ± 0.2	-2	6.0 ± 0.05	+2
Tb	0.7	0.5 ± 0.3	-29	0.3 ± 0.2	-43
Tm	0.4	0.28 ± 0.02	-30	0.36 ± 0.02	-10
Y	19	18.0 ± 0.5	-5	17 ± 1	-11
Yb	1.9	1.72 ± 0.01	-10	1.7 ± 0.2	-11

[a] Acid digestion.

[b] Fusion.

TABLE 4-103. USGS GSP-1 GRANODIORITE

Element	Expected	Observed	% Bias
Ce	360	432 ± 2	+20
Dy	5.7	5.8 ± 0.2	+2
Er	3	1.7 ± 0.1	-43
Eu	2.4	2.16 ± 0.02	-10
Gd	15	12.4 ± 0.3	-17
Ho	-	1.00 ± 0.02	--
La	195	188 ± 1	-4
Lu	0.2	0.16 ± 0.04	-20
Nd	190	206 ± 0.5	+8
Pr	50	56 ± 1	+12
Sm	25	27.4 ± 0.1	+10
Tb	1.4	0.4 ± 0.4	--
Tm	-	0.22 ± 0.06	-17
Y	29	24.0 ± 0.2	--
Yb	1.9	1.40 ± 0.01	-26

[a] Acid digestion.

of trace elements collected on air filters. EMSL-Las Vegas (LV) has prepared guidelines for contractors conducting ICP-AES analyses of samples collected as part of hazardous waste site investigations (U.S. EPA 1981b). EMSL-Cincinnati (Ci) has coordinated the development of a protocol for ICP-AES analysis of elements in surface water, drinking water, and domestic and industrial wastewaters.

The ASTM ICP-AES proposed method covers the determination of 17 dissolved metals in water and wastewater. Calibration with a series of four mixed-element standards is discussed. Other important information needed to perform the analyses is not given or is poorly described. The method has not been validated and no acceptance criteria for precision and accuracy are given. Upper and lower quantitation limits given in the method are presented in Table 4-104.

EMSL-RTP has developed an ICP-AES standard operating procedure (SOP) for determining 48 trace elements in suspended particulate matter collected on glass-fiber filters from the Inhalable Particulate (IP) Network (U.S. EPA 1981a). The procedure is written in protocol fashion under document-control format. The elements are solubilized in a mixture of nitric and hydrochloric acids using heat and ultrasonication. The extent of solubilization of particulate mass is not given. Considerable detail is given with regard to range, sensitivity, detection limits, interferences, preparation of standards and samples, calibration, quality control, and data validation. Many of the analytical details and data-handling instructions are specific to the Jarrell Ash Simultaneous ICP-AES and the minicomputer interfaced with it. As such, the protocol is not directly applicable to other matrices and to other instruments. The data output is processed by the computer into microgram of element per cubic meter of air sampled. The PDP-8E controlling the instrument is interfaced with a PDP-11/34 to achieve data storage capability.

Instrumental detection limits are computed as three times the standard deviation of outputs for the repeated measurement of an acidified reagent blank. Detection limits computed during a sample analysis period (several days to a month) are compared to previously determined values. Detection limits shown in Table 4-105 were obtained from 100 random determinations of this standard over a 4-week period. Upper quantitation limits are also shown.

TABLE 4-104. UPPER AND LOWER QUANTITATION LIMITS FOR ELEMENTS ADDRESSED IN ASTM COMMITTEE D-19 ICP-AES PROPOSED METHOD

Element	Lower limit (μg/L)	Upper limit (μg/L)
Ba	2	10
Be	0.5	10
Cd	1	10
Ca[a]	20	1,000
Co	3	10
Cu	10	10
Fe	3	10
Pb	10	10
Li	4	100
Mg	4	100
Mn	4	100
Mo	10	10
Si	5	100
Sr	0.5	10
V	6	10
Zn	3	10
Na[a]	200	1,000

[a] Using two wavelengths.

TABLE 4-105. EMSL-RTP ICP-AES PROTOCOL CONCENTRATION RANGE[a]

Element	Range (μg/L)	Element	Range (μg/L)
Al	10-5,000	Nb	4-2,000
As	5-5,000	Ni	7-5,000
Au	6-5,000	P	60-20,000
B	15-10,000	Pb	11-25,000
Ba	1.2-10,000	Pd	90-5,000
Be	0.2-2,000	Pt	50-5,000
Bi	300-10,000	Re	140-10,000
Ca	10-40,000	Rh	580-5,000
Cd	2-4,000	Ru	1,200-10,000
Ce	30-5,000	Sb	5-5,000
Co	14-5,000	Se	50-5,000
Cr	7-4,000	Si	60-5,000
Ca	9-20,000	Sm.	22-5,000
Fe	14-50,000	Sn	30-5,000
Ge	80-5,000	Sr	4-5,000
Hg	20-5,000	Ta	9-5,000
In	30-5,000	Te	10-5,000
K	70-20,000	Ti	3.4-5,000
La	7-2,000	Tl	70-5,000
Li	0.8-2,000	V	3-5,000
Mg	6-40,000	W	40-5,000
Mn	2-10,000	Y	1-5,000
Mo	6-5,000	Zn	30-20,000
Na	160-80,000	Zr	6-5,000

[a] Lower detection limits based on December 1979 NAMS analyses. Upper limits based on historical experience, not necessarily instrumental limitations.

Precision and bias of the method have been determined for several elements by the analysis of spiked filter strips (Table 4-106) and for analysis of blind sample replicates (Table 4-107).

Spectral interferences resulting from one element producing a finite output on channels assigned to another element are corrected for by subtracting the interference concentration from the apparent concentration. Correction factors have been tabulated for the elements known to be interferents for IP Network samples. The true concentration of interfering elements also must be known.

Detailed instructions are given for the preparation of all 48-element master standards and for the five separate mixed-element working standards. Correction of calibration-curve nonlinearity observed for certain elements at high concentration (generally >50 mg/L) is discussed.

Detailed instrument operating instructions are given from instrument startup through data validation. Although there are few operator computations required, the operator must evaluate element response during standardization to determine if values are acceptable.

One high- and one low-concentration quality control (QC) solution are used to assess instrument calibration stability. Each solution contains all 48 elements and is analyzed alternately every 10th sample. The PDP has stored expected values for these samples, as well as acceptance criteria based on experience, and performs the relevant comparisons upon receipt of the QC data. At the same time, a cathode ray tube (CRT) displays any indication of out-of-control response. The operator must decide if the specific element out of control merits corrective action. Corrective action may involve correction of short- and long-term instrumental drift, leaks, and torch/spray chamber contamination. After correction, the instrument requires restandardization, as well as reanalysis of the QC solutions and the previous 10 samples.

The December 3, 1979, Federal Register describes an ICP-AES method for determination of 25 elements. This method is updated in the October 26, 1984, Federal Register and has been published as EPA Method 200.7. Development of the method was coordinated by EMSL-Ci. This method may be used for the determination of dissolved, suspended total, or total recoverable elements in surface water, drinking water, and domestic and industrial

TABLE 4-106. RECOVERY OF ELEMENTS FROM SPIKED AIR FILTERS

Element	% Recovery[a]	Standard deviation
As	97	3
Co	96	3
Cu	76	4
Fe	98	4
Mn	97	4
Ni	97	4
Pb	99	2
Sr	96	4
V	94	2
Zn	89	6

[a] Recovery values based on x-ray fluorescence analytical values taken as "true." Data shown were obtained from the analysis of 10 spiked strips analyzed with 1980 NAMS samples during the period July through September 1980.

TABLE 4-107. TYPICAL PRECISION AND BIAS OBTAINED BY SAMPLE/REPLICATE PAIR ANALYSIS[a]

Element	Number of pairs	Coefficient of variation (%)	Bias (%)
As	19	22	1
Co	4	12	-18
Cu	32	16	-6
Fe	32	12	-3
Mn	32	10	-7
Ni	28	17	-20
Pb	32	9	-4
Sr	32	11	-5
V	31	10	-7
Zn	32	14	-7

[a] Data based on the analysis of 32 sample/replicate pairs of 1980 NAMS filters during the period July through September 1980.

wastewaters. Sample preparation procedures for each of these forms of the elements are described. Because of differences between instruments, no detailed instrumental operating conditions are provided. The ICP-AES must be computer-controlled with background correction capability. Recommended wavelengths, typical estimated instrumental detection limits (Table 4-108), potential matrix interferences, and instructions for appropriate corrections are given. Preparation of reagents and master and mixed-element calibration standards are discussed. Both reagent blanks (acid matrix and other reagents used in sample processing) and calibration blanks (HNO_3/HCl to flush system between standards and samples) are used. Five mixed-element calibration standards are used: I--Mn, Be, Cd, Pb, Zn; II--Ba, Cu, Fe, V, Co; III--Mo, Si, As, Se; IV--Ca, Na, K, Al, Cr, Ni; V--Sb, B, Mg, Ag, Tl. An instrument-check standard prepared by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves is analyzed with every 10 samples, and is used to determine instrumental drift. Agreement must be within ±2 percent of the expected values.

Interelement- and background-correction factors are verified by analyzing a real-world sample spiked with the elements of interest at 100 mg/L. Values should fall within 1.5 times the standard deviation of the mean value of this sample.

Weekly analyses of outside reference samples of known concentration are also recommended. A sequence for analyzing samples is given. Mixed calibration standards are run followed by calibration blanks, instrument-check standards, and samples, with calibration blanks between each sample.

Precision and accuracy data are given in Table 4-109 from an interlaboratory study in which seven laboratories analyzed spiked acid-distilled water matrices. Only 14 of the 25 elements were evaluated.

In support of the Superfund Act, EMSL-LV administers a QA program for contract laboratories performing analyses of samples collected during hazardous waste site investigations. While EPA does not require that these contractors follow a specific ICP-AES protocol for the required determination of 17 elements, sufficient detailed guidance is given to qualify this as a QC protocol for ICP-AES analyses. No standardized calibration procedure is

TABLE 4-108. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS FOR FEDERAL REGISTER ICP-AES METHOD

Element	Wavelength[a] (nm)	Estimated detection limit[b] (μg/L)
Aluminum	306.2	45
Arsenic	193.7	53
Antimony	206.833	32
Barium	455.5	2
Beryllium	313.0	0.3
Boron	249.8	5
Cadmium	226.5	4
Calcium	317.9	10
Chromium	267.7	7
Cobalt	228.6	7
Copper	324.7	6
Iron	259.9	7
Lead	220.3	42
Magnesium	279.1	30
Manganese	257.6	2
Molybdenum	202.0	8
Nickel	231.6	15
Potassium	766.4	--[c]
Selenium	196.0	75
Silica (SiO_2)	288.1	27
Silver	328.0	7
Sodium	589.0	29
Thallium	190.864	40
Vanadium	292.4	8
Zinc	213.8	2

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for interferences.

[b] The estimated instrumental detection limits are taken from Inductively Coupled Plasma--Optical Emission Spectroscopy Prominent Lines, EPA-600/4-79-017. Detection limits are sample- and sample-matrix-dependent.

[c] Highly dependent on instrumental operating conditions.

TABLE 4-109. ICP-AES PRECISION AND ACCURACY DATA USING FEDERAL REGISTER METHOD (μg/L)

Element	True value	Mean reported value	% Bias	% RSD
		SAMPLE NO. 1		
Be	750	733	-2	6
Mn	350	345	-1	3
V	750	749	0	2
As	200	208	+4	8
Cr	150	149	-1	4
Cu	250	235	-6	5
Fe	600	594	-1	3
Al	700	696	-1	6
Cd	50	48	-4	12
Co	500	512	+2	10
Ni	250	245	-2	6
Pb	250	236	-6	16
Zn	200	201	+1	6
Se	40	32	-20	22
		SAMPLE NO. 2		
Be	20	20	0	10
Mn	15	15	0	7
V	70	69	-1	3
As	22	19	-14	23
Cr	10	10	0	18
Cu	11	11	0	40
Fe	20	19	-5	15
Al	60	62	+3	33
Cd	2.5	2.9	+16	16
Co	20	20	0	4
Ni	30	28	-7	11
Pb	24	30	+25	32
Zn	16	19	+19	45
Se	6	8.5	+42	42
		SAMPLE NO. 3		
Be	180	176	-2	5
Mn	100	99	-1	3
V	170	169	-1	1
As	60	63	+5	17
Cr	50	50	0	3
Cu	70	67	-4	8
Fe	180	178	-1	6
Al	160	161	+1	13
Cd	14	13	-7	16
Co	120	106	-12	21
Ni	60	55	-8	14
Pb	80	80	0	14
Zn	80	82	+3	9
Se	10	8.5	-15	8

provided, because of differences among brands and models of instruments. The protocol recommends that sensitivity, instrument detection limits, precision, linear dynamic range, and interference effects be investigated and established for each individual element line on each instrument. The protocol requires documentation of instrument calibration (as well as documentation of contractor instrument performance, on daily EPA check standards run to ensure that the calibration is still valid), reagent blank analyses, matrix spike analyses, duplicate sample analyses, and interference check standards. In addition, contractors are required to analyze preaward and quarterly blind performance evaluation samples in water and graphite matrices.

The data quality requirements for the determination of elements in soil, sediment, sludge, waste, and water samples are summarized below:

- Detection Limits are reported to EPA for all instruments and methods that are used by the laboratory and are to be determined no more than 30 days before beginning analyses. Detection limits are reported with all data.
- Calibration. Initial calibration is made using three different concentrations encompassing the range of interest plus a reagent blank. In each 8-h shift, a calibration standard solution is run and the results recorded. In addition, calibration solutions of 25 and 75 percent of the calibration range are analyzed before, after, and in an alternating fashion between every 10 samples.
- Reagent Blank. This blank is processed once every 20 samples or each time a set of samples is analyzed, whichever is more frequent, and the results reported to EPA.
- Laboratory Control Standard is processed through the entire analytical scheme, once for each 8-h shift, and the results reported to EPA.
- Interference Check Standard is run once every 8-h shift and the results reported to EPA.
- Matrix Spike Analyses are performed on the first four samples or 20 percent of those in a set of samples, whichever is smaller.
- Duplicates are analyzed once every 20 samples or with each sample set, whichever is more frequent.

The laboratory control standard results, expressed in terms of the percentage of true values, must fall within the control limits set by EPA (Table 4-110). Matrix spike analyses are required for 5 percent of all samples analyzed. Spiking is carried out by adding elements at twice the endogenous level and a minimum of 10 times the detection limit. Spike recoveries must be within the range set by EPA (Table 4-111). If matrix effects are found to be responsible for unsatisfactory recoveries, then the method of standard additions must be used for all samples of the type involved.

An interference check standard is analyzed at the beginning, end, and at least once for every 20 samples during the sample run to verify on a regular basis interelement and background correction factors. A representative field sample or digest containing low concentrations of the elements of interest, but known concentrations of interfering elements, is spiked with the elements of interest at 100 μg/L or higher levels as appropriate. This sample initially should be analyzed repetitively at least five times to establish a mean value and standard deviation. Values should fall within 1.5 times the standard deviation of this mean value. Examples of analyte and interferent concentrations are shown in Table 4-112.

Instrumental detection limits in micrograms/liter or milligrams/kilogram (Table 4-113) are defined as three times the standard deviation for a calibration blank solution from three nonconsecutive analysis days with at least 10 measurements per day.

TABLE 4-110. ACCEPTANCE LIMITS FOR ANALYSIS OF LABORATORY CONTROL STANDARD

Element	% of true value (EPA set) Low limit	High limit
Aluminum	85	115
Barium	84	116
Beryllium	87	113
Boron	84	116
Cadmium	80	120
Calcium	90	110
Chromium	88	112
Cobalt	78	122
Copper	83	117
Iron	88	112
Lead	78	122
Magnesium	87	113
Manganese	90	110
Nickel	89	111
Sodium	80	120
Vanadium	90	110
Zinc	75	125

TABLE 4-111. ACCEPTANCE LIMITS FOR ANALYSIS OF MATRIX SPIKE SAMPLES

Element	% of true value (EPA set) Low limit	High limit
Aluminum	80	120
Barium	90	110
Beryllium	90	110
Boron	80	120
Cadmium	90	105
Calcium	90	110
Chromium	90	110
Cobalt	90	110
Copper	90	110
Iron	90	110
Lead	88	112
Magnesium	90	110
Manganese	90	110
Nickel	88	112
Sodium	90	110
Vanadium	85	115
Zinc	90	110

TABLE 4-112. EXAMPLE INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATION RATIOS USED FOR INTERFERENCE MEASUREMENTS

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1,000
B	10	Ca	1,000
Ba	1	Cr	200
Be	1	Cu	200
Ca	1	Fe	1,000
Cd	10	Mg	1,000
Co	1	Mn	200
Cr	1	Ni	200
Cu	1	Ti	200
Fe	1	V	200
Mg	1		
Mn	1		
Na	10		
Ni	10		
Pb	10		
V	1		
Zn	10		

TABLE 4-113. DETECTION LIMITS FOR ELEMENTS DETERMINED BY ICP-AES UNDER EMSL-LV QA PROGRAM

Element	Detection limits (μg/L)
Al	50
Cr	10
Ba	10
Be	2
Cd	5
Co	10
Cu	20
Fe	20
Pb	40
Ni	20
Mn	10
Zn	10
B	10
V	10
Ca	100
Mg	100
Zn	100

SECTION 5

DIRECT CURRENT PLASMA EMISSION SPECTROSCOPY

5.1 OPERATING PRINCIPLES OF DC PLASMAS

The direct current (DC) plasma (sometimes called a plasma jet) is formed by applying a direct current to a set of electrodes through which high purity (99.995 percent) argon gas is passed. The resulting plasma jet is then sustained by the continuous passage of argon and the maintenance of around 7 to 14 A and 1 kW of current. The electrodes are cooled by a flowing water supply. Two plasma configurations have been used in DCP-AES. The first, the inverted V configuration (Figure 5-1), is no longer used in current instrumentation. The second, the inverted Y configuration (Figure 5-2), is the one used in current instrumentation. The two-electrode plasma source produced a plasma that drifted excessively. A third electrode was added (shown in Figure 5-2) to stabilize the plasma. The plasma jet formed between the two anodes is held stable by the cathode located above the anodes.

In both configurations, the sample, which has been converted to an aerosol by nebulization into a spray chamber, is forced upwards by a peristaltic pump and an argon carrier-gas flow at 1 to 3 L/min into the zone just below the confluence of the two anodal plasmas. The maximum residence time of the aerosol in the plasma occurs in this region (Fairless 1978). This area, the sample excitation region, experiences a temperature of around 4,500 to 6,000 K, whereas in the current core, temperatures may exceed 14,000 K. The emission spectra produced by the sample are viewed in this region because of the lower background emission relative to other locations within the plasma.

In the three-electrode system, the electrodes consist of two graphite anodes and one thoriated tungsten cathode. The electrodes are positioned within ceramic sleeves, which are kept from melting by the high-velocity

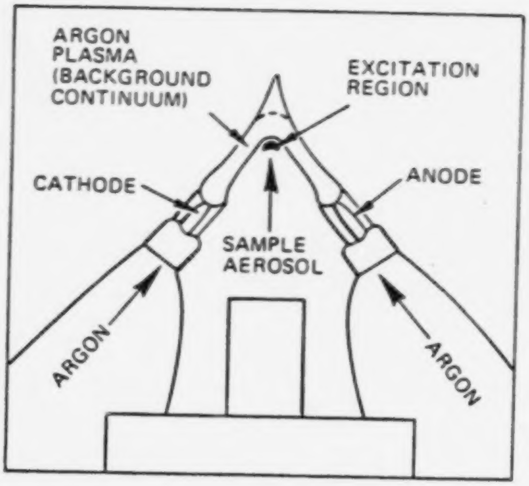
ARGON
PLASMA
(BACKGROUND
CONTINUUM)
EXCITATION
REGION
CATHODE
ANODE
SAMPLE
AEROSOL
ARGON
ARGON

Figure 5-1. Schematic of two-electrode DC plasma © 1986, courtesy of Beckman Instruments/ Instrumentation Laboratory.

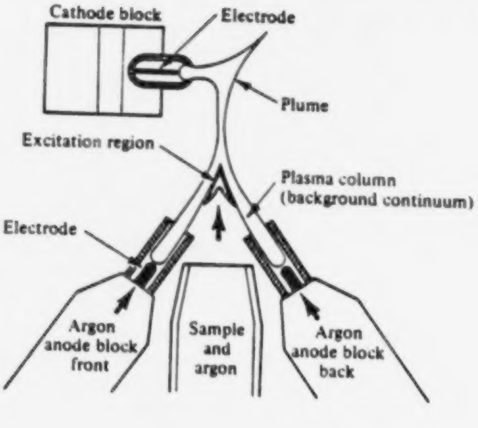
Cathode block
Electrode
Plume
Excitation region
Plasma column
(background continuum)
Electrode
Argon
anode block
front
Sample
and
argon
Argon
anode block
back

Figure 5-2. Schematic of three-electrode DC plasma © 1986, courtesy of Beckman Instruments.

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flow of argon gas. The electrodes eventually wear down and must be replaced. The spacing between them determines the plasma configuration, so they must be adjusted periodically (Kahn et al. 1979a; Willard et al. 1981). The argon flow rates to the anode and cathode are around 1.2 to 1.5 L/min, and around 5 to 6 L/min to the nebulizer; a total argon gas consumption of around 10 L/min. This can be contrasted with an ICP's total argon flow of around 10 to 20 L/min, most of which is used to sustain and support the plasma.

5.2 SAMPLE PREPARATION PROCEDURES

The discussion provided for the inductively coupled plasma is generally applicable to the DC plasma. The DC plasma is said to be more tolerant of particulate-laden matrices and nonaqueous liquid samples, but the small data base cannot confirm this. The following are examples of sample preparation approaches used in DCP analyses.

Bankston et al. (1979) used a sequential DCP-AES to determine major and minor elements in silicate rocks. Previously ground rock samples (0.2 g) and $LiBO_2$ (1.4 g) are mixed together and fused in a graphite crucible at 950 °C for 14 min, after which the fusion melt is dissolved in 75 mL of a 0.25 percent (w/v) solution of CsCl and brought to 100 mL total volume with the same CsCl solution. This solution contains Cs at a concentration of 0.2 percent (w/v) and is used for all determinations except Na_2O and K_2O, which require a 0.32 percent (w/v) Cs concentration. Major amounts of easily ionized elements have the net effect of increasing the analytical sensitivities of the other elements present in a way that is concentration dependent and thus is subject to vary from sample to sample. The Cs is added to equalize these ionization enhancements of major element signals that occur in the DC plasma. $LiBO_2$ alone is not sufficient. USGS and Canadian Certified Reference Materials Project rock standards are used for calibrations. Results for analyses of silicate rocks for major and minor elements are given in Tables 5-1 and 5-2. Detection limits for trace elements are given in Table 5-3.

Cantillo et al. (1984) used a sequential DCP-AES to determine major and minor elements in sediment sample after $LiBO_2$ fusion. Sediment samples

TABLE 5-1. ANALYSES OF FIVE STANDARD REFERENCE ROCKS FOR MAJOR OXIDE COMPOSITION (as weight %)

	Basalt ZGI-BM		Granite CRPG-GH		Periodotite USGS PCC-1		ANRT DR-N		Syenite NIM-S	
Oxide	Found	Published	Found	Published	Found	Published	Found	Published	Found	Published
SiO_2	50.86	49.60[a]	76.37	75.80[a]	42.78	41.90[b]	51.87	52.65[a]	62.47	63.72[c]
Al_2O_3	16.42	16.20[a]	11.58	12.50[a]	0.78	0.74[c]	17.77	17.42[a]	16.47	17.33[c]
Fe_2O_3	9.36	9.68[c]	1.40	1.34[a]	8.59	8.35[c]	9.66	9.91[c]	1.63	1.40[c]
MgO	7.38	7.46[c]	0.09	0.03[a]	43.71	43.18[c]	4.24	4.50[a]	0.50	0.48[c]
CaO	6.75	6.44[c]	0.53	0.69[a]	0.43	0.51[c]	7.24	7.08[a]	0.55	0.70[c]
Na_2O	4.98	4.64[c]	3.88	3.85[a]	ND[d]	0.006[b]	2.95	3.00[a]	0.46	0.43[c]
K_2O	0.10	0.20[c]	4.88	4.76[a]	ND	0.004[b]	1.77	1.70[a]	15.53	15.34[c]
TiO_2	1.14	1.14[c]	0.12	0.08[a]	ND	0.015[b]	1.07	1.11[a]	0.10	0.05[c]
P_2O_5	0.09	0.11[c]	0.03	0.01[a]	ND	0.002[b]	0.24	0.27[a]	0.14	0.13[c]
MnO	0.14	0.15[c]	0.05	0.05[a]	0.13	0.12[a]	0.24	0.21[a]	0.01	0.01[c]

[a] Recommended value.

[b] Magnitude.

[c] Average value.

[d] ND = none detected.

TABLE 5-2. CONCENTRATIONS (as μg/g) OF SEVEN TRACE ELEMENTS IN FIVE REFERENCE ROCKS

Element	Basalt ZGI-BM		Granite CRPG-GH		Peridotite USGS PCC-1		Diorite ANRT DR-N		Syenite NIM-S	
	Found	Published	Found	Published	Found	Published	Found	Published	Found	Published
Ba	269	263[a]	20	22[a]	<10	1.2[b]	387	360[a]	2,503	2,590[b]
Cr	143	123[a]	5	6[c]	2,521	2,730	35	45[a]	6	13[b]
Cu	42	45[a]	<2	12[a]	18	11.3[b]	50	52[b]	27	23[b]
Ni	35	57[a]	3	3[a]	2,380	2,339[b]	3	16[a]	8	8[b]
Sr	228	230[a]	4	10[a]	<3	0.41[a]	381	400[a]	86	76[b]
V	207	180[a]	<10	5[c]	34	30[b]	205	225[a]	17	10[b]
Zn	115	107[b]	57	80[a]	60	36[a]	148	150[a]	17	21[b]

[a] Recommended value.

[b] Average value.

[c] Magnitude.

TABLE 5-3. DETECTION LIMITS FOR TRACE ELEMENT DETERMINATION

Elemental analyte	Limit of detection[a]	Elemental analyte	Limit of detection[a]
Ba	10	Sr	3
Cr	10	V	10
Cu	2	Zn	15
Ni	3		

[a] μg/g of rock.

(0.2 g) were weighed into a small depression in 1.0 g of $LiBo_2$ in a graphite crucible. Placing the sample in the depression was considered necessary to prevent incomplete fusion, which was endountered when sediments are in direct contact with the graphite. During the fusion, the crucibles lose up to 10 percent of their initial mass, part of which is trapped in the molten borate, resulting in insoluble black particles in the final solution. The sediment-flux mixture is fused in a muffle furnace at 950 ± 50 °C for 15 min, the minimum time required to achieve a successful fusion. The liquid borate melt is then poured into 100 mL of 5 percent HNO_3, mixed, and the resulting solution analyzed by DCP-AES for the elements given in Table 5-4 at the indicated wavelengths. Somewhat lower detection limits can be achieved by using more sample (while keeping the flux-sample ratio the same) or by reducing the final volume. The precision of the method was evaluated by analyzing 10 geochemical reference standards. Data for the analyses of USGS marine mud and NBS estuarine sediment SRM 1646 are given in Tables 5-5 and 5-6, respectively. Fusion of NBS river sediment SRM 1645 produced an insoluble residue thought to be chrome magnetite, resulting in lower recoveries for Cr (71 percent) and Fe (68 percent). A similar problem occurred with the NRC marine sediment MESS-1. Results for all sediments for Mo and Nb were unacceptable, due to spectral background and wavelength coincidences that could not be corrected for with the instrument used. W could not be determined due to unexplained reasons. This instrument lacks wavelength scanning capability that is needed to carry out such corrections. The analysts were also unable to successfully predict interference problems by inspecting standard wavelength table compilations.

Hunter et al. (1981) determined Al, Fe, Ca, and Mg in wet-process phosphoric acid by DCP-AES. A paired t-test showed no significant difference between this method and AAS at the 95-percent confidence level.

5.3 SAMPLE INTRODUCTION TECHNIQUES

The discussion provided for the inductively coupled plasma is generally applicable to the DC plasma. The small data base indicates that fewer applications of novel sample introduction techniques like hydride generation and electrothermal atomization have been demonstrated.

TABLE 5-4. EMISSION LINES AND LOWEST DETECTABLE CONCENTRATIONS IN SEDIMENT[a]

Element	Emission line[b], nm	Lowest detectable concentration in sediments[c]	Element	Emission line, nm	Lowest detectable concentration in sediments
Al	396.2	3 (mg/g)	Ga	417.2	2
Si	288.2	3 (mg/g)	Y	371.0	2
Ti	334.9	0.04 (mg/g)	Zr	339.2	6
V	347.9	5	Nb	408.0	
Cr	357.9	2	Mo	379.8	
Mn	403.1	10	La	394.9	5
Fe	373.7	0.4	Ce	418.7	10
Co	340.5	7	Dy	353.2	1
Ni	341.5	2	Yb	369.4	1
Cu	324.8	2	W	400.9	
Zn	213.9	5	Tl	351.9	

[a] Expressed in μg/g except where indicated by (mg/g).

[b] Wavelengths are reported only to 0.1 nm because of the physical limitations of setting the monochromator.

[c] Composition on a dry weight basis that will produce a solution by the described procedure with a concentration that will produce a signal twice the average standard deviation after subtraction of the blank.

TABLE 5-5. COMPARISON OF REPLICATE ANALYSIS OF THE MARINE MUD (MAG-1)

Element[a]	Analyzed simultaneously (n = 6)[b]	Analyzed over 10 months (n = 15)[c]
Al(%)	7.6(<1)[d]	7.0(10)[d]
Si(%)	24(<2)	23(5)
Ti(%)	0.48(4)	0.49(6)
V	140(<4)	140(4)
Cr	89(1)	94(6)
Mn	690(3)	670(3)
Fe(%)	4.4(2)	4.1(8)
Co	26(12)	28(24)
Ni	53(4)	53(6)
Cu	33(10)	32(9)
Zn	120(4)	120(8)
Ga	28(3)	27(11)
Y	11(7)	13(19)
Zr	98(2)	110(7)
La	41(2)	42(17)
Ce	130(6)	110(13)
Dy	3.0(10)	3.6(22)
Yb	1.6(6)	2.3(23)

[a] Dry weight except where percent.

[b] Mean values of 6 samples analyzed together as a batch.

[c] Mean values of 15 samples analyzed one at a time over a period of 10 months.

[d] Coefficient of variation (%) = 100 σ/mean.

TABLE 5-6. FUSION RESULTS OF DUPLICATE ANALYSES OF THE NBS ESTUARINE SEDIMENT (SRM-1646)[a]

Element	Analyst I (n = 6)[b]	Analyst II (n = 15)[c]
Al(%)	5.3(2)[c]	5.4(1)
Si(%)	30(3)	30(1)
Ti(%)	0.36(2)	0.37(2)
V	89(3)	91(3)
Cr	74(1)	70(4)
Mn	280(2)	280(2)
Fe(%)	2.9(2)	3.0(0)
Co	17(18)	20(14)
Ni	31(5)	37(6)
Cu	28(9)	28(6)
Zn	130(0)	120(13)
Ga	19(8)	19(6)
Y	17(8)	15(4)
Zr	270(4)	300(4)
La	36(2)	36(3)
Ce	110(4)	110(7)
Dy	2.8(7)	3.1(14)
Yb	2.2(4)	2.0(5)

[a] μg/g except where percent.

[b] Number of samples.

[c] Coefficient of variation (%) = 100 σ/mean.

5.4 ELEMENT IDENTIFICATION AND QUANTITATION

5.4.1 Detection Systems

The small viewing zone (excitation region) in the DC plasma jet required the developers of DC plasma spectrometers to select a detector system capable of magnifying and dispersing the radiation produced (Decker 1981). As a result of this requirement, the detector system chosen was an echelle spectrometer equipped with photomultiplier tubes. An echelle is a coarsely ruled grating or dispersion device with 8 to 300 grooves/mm compared with 300 to 3,600 grooves/mm for conventional gratings (Zander 1982). The coarsely ruled grating produces high orders of interference and great dispersion of the emission being viewed (an order of interference is the difference in the number of wavelengths along the path of two constructively interfering rays of light). For a 79-groove/mm echelle grating, orders of 118 to 28 are used to cover the range from 200 to 800 nm. To simplify the highly ordered spectrum that is produced, a prism is placed before the grating to sort the spectral orders in a stacked two-dimensional rectangular pattern within an 8- by 8-cm array. The prism separates the wavelengths in a vertical direction while the grating separates them horizontally. Placed side by side, these orders would result in a focal length requirement of 6.5 m for the spectrometer. However, due to the stacking of orders, the 0.75-m focal length of the echelle spectrometer is sufficient. A small entrance slit is used to eliminate order overlap.

A schematic of an echelle spectrometer is shown in Figure 5-3. The resultant dispersion and resolution of the echelle spectrometer is 5 to 10 times greater than that of a conventional monochromator (Beckman Instruments 1980).

The echelle spectrometer can be operated in three modes. For qualitative analysis, a special camera arrangement is used to photograph the radiation produced by the echelle grating/prism. The resulting emission lines on the photograph are then compared with known elemental lines using a clear plastic overlay (Willard et al. 1981; Beckman Instruments 1980). For quantitative sequential analysis, the echelle is operated as a scanning monochromator. Both the spectral orders and the wavelength within an order must be selected for each element.

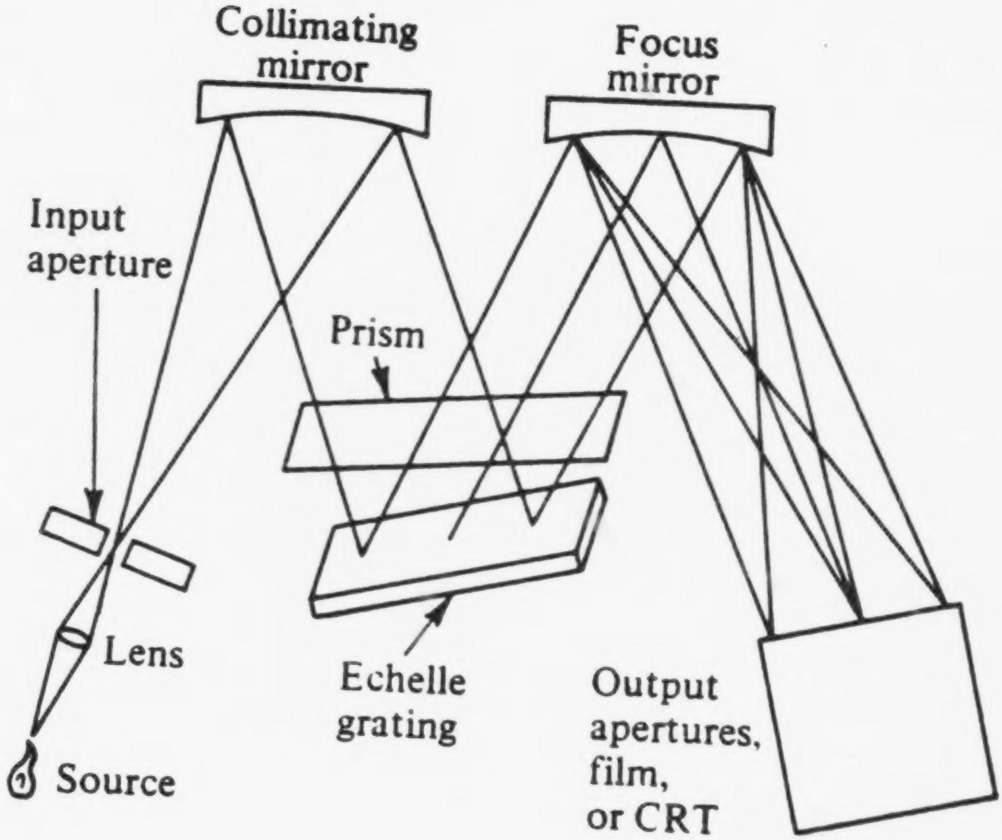
Collimating mirror
Focus mirror
Input aperture
Prism
Lens
Source
Echelle grating
Output apertures, film, or CRT

Figure 5-3. Echelle grating spectrometer © 1986, courtesy of Beckman Instruments.

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A multichannel cassette is used for simultaneous determination of up to 20 elements. This module consists of photomultiplier tubes fixed to the exit slits on a removable framework (Figure 5-4).

5.4.2 Interferences

Correction for spectral background in the DCP emission is made by moving a quartz refractor plate to shift the spectrum onto the exit slit. The correction of spectral interferences due to direct spectral overlap was not described, but because all DCP spectrometers are scannable, an alternate wavelength should usually be available.

Chemical suppression interference of Ca by P was observed with the two-electrode jet (Zander 1982; Skogerboe and Urasa 1978), but not with the three-electrode DCP.

A more significant interference in the DCP is the enhancement of emission line intensities due to the presence of easily ionizable elements such as alkali metals present at >0.1 percent. This effect has been reported by several investigators (Nygaard 1979; Decker 1981) and has been studied by Eastwood et al. (1980) who found that there was a relationship between the energy of transition for the atomic line and the number of unpaired d-electrons in the lower atomic state. This relationship could be used to predict the differences in relative signal enhancement for 14 elements in seawater, although the relationship may not be valid for other elements and matrices. The advantage of this enhancement effect, increasing the sensitivity of the detector to a particular set of emission lines, is offset by the need to match matrices, blanks, and standards by standard addition methods or by using excitation buffers such as Li to compensate for the enhancement effect. Because this enhancement has not been found to be a simple phenomenon, its correction by either of these approaches is not always successful.

Because the DCP produces primarily atomic rather than ionic lines in the excitation region, the spectral line intensity compilation choices to use for reference are quite limited (Zander 1981). The Fassel and Boumans compilations are specific to the ICP and are of no use in DCP work. The best available tabulation for DCP is the NBS Tables of Wavelengths, although these are based on approximations and not actual measurements made with a

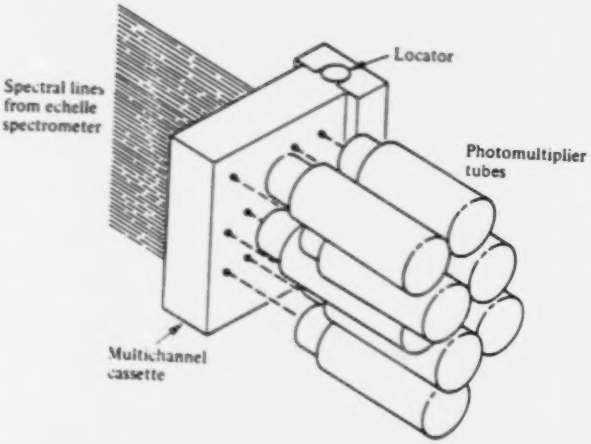
Locator
Spectral lines from echelle spectrometer
Photomultiplier tubes
Multichannel cassette

Figure 5-4. Echelle spectrometer operated as a direct reader © 1986, courtesy of Beckman Instruments.

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DCP. For example, although the line locations may be identical, the character of the line-intensity fluctuations and broadening may be different.

5.4.3 Data Processing

The DCP spectrometer uses a microprocessor-controlled computer to calibrate the instrument, convert emission intensities to concentrations, integrate emission signals, subtract blanks and spectral background, and calculate mean values and standard deviations.

5.5 ELEMENTAL COVERAGE

The sparse published data for DCP spectroscopy indicate that up to 64 elements have been determined (Reednick 1979; Decker 1981), but not all in the same sample. The design of the DCP direct reader is such that a maximum of 20 elements can be determined per cassette, although it would be possible to use more than one cassette to increase the range of elements covered. The sequential scanning ability of the spectrometer should permit determination of at least 50 elements in a single sample, although this has not been demonstrated and likely will be subject to the same limitations that apply to the ICP spectrometers. Qualitative coverage by the photographic detection system also is limited to the direct reader approach (20 elements).

Coverage capability for specific groups of elements such as hydride formers, rare earths, noble metals, and nonmetals in matrices other than water could not be confirmed.

5.6 DATA QUALITY

5.6.1 Detection Limit

The linear dynamic range of the DCP is around three orders of magnitude, somewhat less than for ICP, which is quoted at around 3 to 5 orders of magnitude. The detection limits for DCP generally are reported as around 10 times higher than for ICP on the same sample (Tables 5-7 and 5-8).

5.6.2 Precision

Both the short-term and long-term precision of the DCP have been measured and compared with that of the ICP. The short-term precision is

TABLE 5-7. COMPARISON OF ICP AND DCP DETECTION LIMITS[a]

Element	Wavelength (nm)	Detection limit (ng mL^{-1})	
		SpectraJet III	ICP
Scandium	361.3	3	0.4
Yttrium	371.0	7	0
Lanthanum	398.8	15	10
Cerium	401.2	40	10
Praeseodymium	422.5	80	10
Neodymium	430.0	200	40
Samarium	392.8	40	40
Europium	420.5	10	2
	382.0	3	--
Gadolinium	364.0	20	7
Terbium	350.9	40	7
Dysprosium	400.0	50	9
Holmium	345.6	200[b]	3
	405.3	80	--
Erbium	369.2	10	3
Thulium	376.1	10	2
Ytterbium	369.4	2	0.4
Luthetium	347.2	100[a]	20

[a] Decker 1981.

[b] Severe spectral interference. The detection limits were estimated visually.

TABLE 5-8. DCP DETECTION LIMITS FOR AQUEOUS SAMPLES
(D.L. = 2 × S.D. of blank)

Element	Detection limit (μg/mL)	Element	Detection limit (μg/mL)	Element	Detection limit (μg/mL)
Ag	0.002	In	0.025	Re	0.015
Al	0.001	Ir	0.040	Rh	0.030
Au	0.002	K	0.010	Ru	0.020
As	0.030	La	0.001	Sb	0.030
B	0.003	Li	0.001	Se	0.030
Ba	0.001	Mg	0.0001	Si	0.010
Be	0.001	Mn	0.001	Sm	0.055
Bi	0.050	Mo	0.001	Sn	0.015
Ca	0.0001	Na	0.001	Sr	0.001
Cd	0.005	Nb	0.025	Ta	0.050
Co	0.002	Nd	0.025	Te	0.050
Cr	0.001	Ni	0.001	Ti	0.002
Cu	0.001	P	0.050	U	0.100
Dy	0.003	Pb	0.015	V	0.005
Er	0.003	Pd	0.006	W	0.020
Fe	0.002	Pr	0.035	Y	0.001
Ga	0.025	Pt	0.017	An	0.001
Hg	0.050	Rb	0.010	Zr	0.005

Source: Reednick, 1979.

defined as that obtained on replicate analyses of a single sample or standard during a calibration period at concentrations of 100 times the detection limit. The long-term precision is defined as that obtained on the same sample analyzed during different calibration periods, generally days apart. The data for each technique are:

- Short-term precision	DCP 0.5-5% RSD ICP 0.5-2% RSD
- Long-term precision	DCP 2-10% RSD ICP 3-10% RSD (Zander 1982)

Thus the short- and long-term precisions for the three-electrode DCP and the ICP are essentially the same.

5.6.3 Accuracy

The accuracy of the DCP spectrometer has been evaluated on analyses of NBS SRMS (Table 5-9), standard water samples (Table 5-10), and standard oils (Tables 5-11 and 5-12). Biases of around 15 percent were observed for these matrices and the elements determined. However, the small data base does not allow general conclusions to be made about the accuracy of DCP spectroscopy.

As indicated by the sparse amount of data presented in this section, there is significantly less DCP-spectrometry data cited in the literature than that available for ICP. The exact reasons for this lack are not clear, but only a small percentage of the existing DCPs are used in research. DCP is are used in routine industrial process monitoring applications, and these data are not published in the literature. Another factor limiting the DCP data base is that there is only one supplier of DCP spectrometers, Beckman Instruments. Because of the nature of the DCP excitation zone, an echelle spectrometer is almost a requirement for DCP analysis. Until recently, Beckman held the only patent on this spectrometer, thus limiting the market for other potential suppliers. Finally, the poor performance of the now-obsolete two-electrode DCP probably discouraged potential users from purchasing the newer DCP spectrometers.

TABLE 5-9. ANALYSIS OF NBS SRMs: SPECTRAJET III[a]

	Natural water[b]		Bovine liver		Pine needles		Orchard leaves		Spinach	
Element	SJIII	NBS	SJIII	NBS	SJIII	NBS	SJIII	NBS	SJIII	NBS
Al	83 ± 2	78 ± 1	--	--	--	--	--	--	--	--
Cr	--	--	0.2 ± .02	--	--	--	2.7 ± .2	2.6 ± .2	4.7 ± .3	4.6 ± .3
Cu	--	--	--	--	3.2 ± .2	3.0 ± .3	--	--	13 ± 1	12 ± 2
Fe	76 ± 2	76 ± 1	--	--	--	--	--	--	--	--
Mn	29 ± 3	29 ± 1	12.5 ± 2	10.3 ± 1	673 ± 10	675 ± 15	92 ± 1	91 ± 4	178 ± 2	165 ± 6
Ni	48 ± 4	48 ± 1	--	--	2.9 ± .1	3.5 (nc)[c]	1.7 ± .1	1.3 ± .2	1.3 ± .1	6 (nc)
V	50 ± 2	50 ± 1	--	--	--	--	--	--	1.08 ± .07	--
Zn	61 ± 1	65 ± 3	141 ± 2	130 ± 10	71 ± 1	--	28 ± 1	25 ± 3	52 ± 1	50 ± 2

[a] Data submitted by D. Sutton and R. Morse, U.S. Department of Energy.

[b] Values are μg/g except for natural water, which is ng/mL.

[c] (nc) = Noncertified value given by NBS.

TABLE 5-10. TRACE METALS IN WATER--ASTM REFERENCE STANDARD
(values in mg/L)[a]

Element		SJIII	ASTM[b]	SJIII	ASTM	SJIII	ASTM
Cu	a-H_2O[c]	0.4	0.4	2.0	2.0	3.9	4.0
	b-H_2O[d]	0.5		1.5		3.9	
Fe	a	4.2	4.4	0.2	0.2	2.3	2.4
	b	4.6		0.2		2.7	
Pb	a	5.4	6.0	7.3	8.0	1.0	1.0
	b	6.3		7.2		0.8	
Mn	a	0.4	0.4	2.1	2.0	4.1	4.0
	b	0.5		2.5		5.7	
Ni	a	8.5	8.0	0.9	0.8	4.1	4.0
	b	7.9		0.7		4.1	
Cd	a	0.7	0.6	1.7	1.6	0.2	0.2
	b	0.5		1.5		0.1	
Cr	a	0.8	0.85	2.9	3.41	5.9	6.82
	b	0.9		2.8		7.1	
Co	a	1.7	1.5	0.2	0.16	0.9	0.8
	b	1.5		0.1		0.9	
Zn	a	3.8	4.0	8.1	8.0	0.9	1.0
	b	5.2		9.3		1.6	

[a] Data obtained from D. Bankston, Woodshole Oceanographic Institute.

[b] ASTM = Value in diluted samples.

[c] a-H = Concentrate diluted with deionized water.

[d] b-H = Concentrate diluted with Saragasso Sea water.

Source: Reednick, 1979.

TABLE 5-11. ACCURACY AND PRECISION OF DCP ANALYSES OF WEAR METALS IN OIL

Element	T = 0	T = 12 h	T = 24 h	T = 36 h	T = 48 h	Mean, S.D.	% RSD
				25 µg/g			
Al	25.4	24.7	25.4	25.5	25.9	24.6 ± .43	1.7
Ni	25.1	24.3	23.5	24.5	24.6	24.4 ± .58	2.4
Fe	25.3	24.6	24.3	25.0	25.1	24.9 ± .42	1.7
Cr	25.0	24.5	24.1	24.7	24.7	24.6 ± .33	1.3
Mg	25.0	24.4	23.9	24.6	24.6	24.5 ± .40	1.6
Cu	25.2	24.6	25.2	25.2	25.3	25.1 ± .28	1.1
Ag	24.8	25.1	25.1	25.2	25.4	25.1 ± .22	0.9
Ti	25.2	24.6	24.4	24.9	25.1	24.8 ± .34	1.4
				5.0 µg/g			
Al	5.41	5.04	5.10	5.17	5.10	5.16 ± .16	2.8
Ni	5.00	5.12	5.06	5.21	4.89	5.06 ± .12	2.4
Fe	5.04	5.08	5.10	5.21	4.94	5.07 ± .10	1.9
Cr	5.03	5.04	5.03	5.13	4.89	5.02 ± .02	1.7
Mg	4.95	5.06	5.00	5.10	4.82	4.99 ± .11	2.2
Cu	5.22	5.02	5.11	5.14	4.87	5.07 ± .13	2.6
Ag	5.17	5.10	5.15	5.21	4.89	5.10 ± .13	2.5
Ti	5.25	5.03	4.97	5.10	4.94	5.06 ± .12	2.4

Source: Reednick, 1979.

TABLE 5-12. ACCURACY AND PRECISION OF DCP ANALYSIS OF ORGANOMETALLICS IN KEROSENE (μg/g)

Element	20.0	10.0	5.0	0.0	D.L.
Ag	19.7 ± 0.08	10.8 ± 0.04	5.65 ± 0.01	0.034 ± 0.013	0.026
Al	19.8 ± 0.09	10.3 ± 0.04	5.15 ± 0.03	0.040 ± 0.016	0.032
Ba	19.9 ± 0.17	9.26 ± 0.06	4.33 ± 0.03	0.076 ± 0.083	0.166
Cd	19.7 ± 0.08	10.2 ± 0.04	5.20 ± 0.04	0.065 ± 0.017	0.034
Cr	19.7 ± 0.08	10.1 ± 0.03	5.02 ± 0.02	0.007 ± 0.10	0.020
Cu	19.5 ± 0.08	10.7 ± 0.05	5.54 ± 0.03	0.036 ± 0.012	0.022
Fe	19.7 ± 0.04	10.2 ± 0.02	5.14 ± 0.02	0.011 ± 0.01	0.02
Mg	19.8 ± 0.06	10.1 ± 0.02	5.09 ± 0.02	0.023 ± 0.016	0.032
Mn	19.7 ± 0.03	10.4 ± 0.02	5.30 ± 0.2	0.020 ± 0.000	0.001
Mo	19.5 ± 0.13	10.5 ± 0.03	5.39 ± 0.03	0.026 ± 0.017	0.034
Na	20.1 ± 0.12	9.98 ± 0.06	4.42 ± 0.10	0.005 ± 0.012	0.024
Ni	19.5 ± 0.08	10.3 ± 0.05	5.14 ± 0.09	0.078 ± 0.040	0.080
Pb	19.4 ± 0.28	10.0 ± 0.12	5.33 ± 0.25	0.104 ± 0.144	0.288
Si	19.5 ± 0.02	10.5 ± 0.09	5.40 ± 0.02	0.034 ± 0.021	0.042
Sn	19.5 ± 0.12	10.4 ± 0.08	5.30 ± 0.02	0.070 ± 0.068	0.136
Ti	19.7 ± 0.11	9.87 ± 0.01	4.82 ± 0.03	0.019 ± 0.013	0.026
V	19.2 ± 0.26	10.7 ± 0.14	5.65 ± 0.05	0.155 ± 0.056	0.112
Zn	20.0 ± 0.04	10.4 ± 0.02	5.20 ± 0.04	0.024 ± 0.022	0.044

5.7 STANDARD OPERATING PROCEDURES

ASTM Committee D-19 has proposed a test method for elements in water by DCP-AES. The proposed method addresses the determination of 15 dissolved and "total recoverable" elements in water and wastewater. Total recoverable elements in this method refers to those elements solubilized by an HNO_3/HCl digestion procedure described in the method. The elements for which the method is said to be applicable are listed in Table 5-13 along with their method detection limits. Many significant details and decisions are left to the discretion of the analyst.

TABLE 5-13. ELEMENTS AND DETECTION LIMITS ADDRESSED IN ASTM COMMITTEE D-19 DCP-AES PROPOSED METHOD

Element	Detection limit (μg/L)
Aluminum	10
Arsenic	200
Barium	10
Boron	5
Cadmium	10
Chromium	5
Cobalt	15
Copper	10
Iron	20
Lead	50
Manganese	10
Mercury	200
Nickel	15
Vanadium	15
Zinc	15

SECTION 6

SPARK SOURCE MASS SPECTROMETRY

6.1 OPERATING PRINCIPLES

Spark source mass spectrometry (SSMS) is, by comparison with plasma emission, a much older technique; its principles and instrumentation having been developed in the 1930's through 1950's. SSMS achieved its greatest popularity in the 1950's and 1960's primarily in the field of materials analysis. Although environmental applications were greatest in the 1960's, the advent of atomic absorption and x-ray spectrometric methods and the increased availability of neutron activation facilities signaled the beginning of a slow decline in SSMS usage that continues today. There are a number of reasons for this; primarily, the cost of instrumentation and needed accessories priced SSMS outside the budgets of all but the largest research universities and government laboratories. Also, significant improvements in operating hardware have not occurred since the early 1960's. Of even greater significance is the perception that SSMS is at best a semiquantitative technique. All of these factors have resulted in SSMS becoming of less interest to analytical chemists, especially those concerned with environmental analyses.

A general description of the operating principles of SSMS is given here and will be followed by a more detailed discussion of the key steps in an SSMS analysis and their affect on the quality of the data produced.

A spark source mass spectrometer is a large and complex instrument requiring a dedicated laboratory to accommodate the instrument and its accessories. It consists of four major components housed within a single framework, with several large subsystems that are connected by cables or wiring to the instrument. The major components are the source, the electrostatic analyzer, the magnetic or mass analyzer, and the detector, which is typically a photographic plate, but may involve some form of electrical detection of the signal.

The sample material, which may require some form of pretreatment (e.g., to remove organics), typically is formed into a set of conducting electrodes with graphite, although any conducting matrix may be used. The electrodes are placed in the ion source, which is then maintained under a high vacuum, generally 10^{-7} to 10^{-8} torr. The rest of the system generally is kept under vacuum to facilitate sample analyses and to reduce possible atmospheric contamination of the analyzers and detector systems. A pulsed radiofrequency (RF) signal of about 4 kV is then applied across the electrodes from an external power supply. When a critical minimum distance between the electrodes is reached, the result is a visible spark discharge producing a cloud of positively charged ions representative of the electrode material.

Due to the somewhat wide and erratic energy spread of the vacuum spark discharge, the nature and number of ions produced may vary considerably over the course of the sparking, requiring some complex focusing and refocusing of the ions to produce a useful signal. This ion cloud is then induced to move from the ion source through an accelerating plate by applying a negative 20-kV voltage to the source plate. The ion cloud is focused into an ion beam by a series of slits that lead into the second major component, the electrostatic analyzer. This analyzer double focuses the ion beam according to both speed and direction. This is known as the Mattauch-Herzog double-focusing design and is characteristic of all modern spark source mass spectrometers. At the end of the electrostatic analyzer, approximately 50 percent of the total charge of the ion beam is collected by a monitor and reported as an ion current in amperes. This information is used by the analyst to determine and regulate the amount of charge entering the detector, which is correlated with the amount of each ion detected at a given exposure. The rest of the ion beam enters a magnetic analyzer where the ions are separated according to mass and charge ratio (m/e) by a constant magnetic field. The heavier, slower ions are deflected more than the lighter, faster ions resulting in a mass/charge spectrum of all elements in the periodic table present in the sample. This spectrum is collected on a photographic plate providing a permanent record, or, if an electrical detection system is used, selected ions are measured as they pass through a slit onto the first dynode of an electron multiplier.

A series of these exposures is made with either a two- or threefold reduction in the amount of charge collected with each subsequent exposure. This series of graded exposures, as recorded on a photoplate, produces a spectrum covering a concentration range of nearly one million. The plates are removed from the instrument, developed, the blackening or intensity of the lines produced is read visually or by an instrument, and is correlated with the concentration of elements and standards in the sample. This data-reduction process ranges in complexity from simple visual interpolation to using complex computer programs that convert spectral transmittance to concentration, and generally is considered the most labor-intensive and time-consuming step of the SSMS analysis.

6.2 SAMPLE PREPARATION PROCEDURES

The need for extensive sample preparation in SSMS is reduced greatly because of the technique's capability of analyzing solid samples. Particulate matter, ash, soil, rocks, or other inorganic solids generally do not require decomposition by use of acids, fusions, or heat prior to their analysis. The key requirements that must be met are:

- The sample must form a stable electrode with the carbon or aluminum matrix.
- The organic content of the sample must be less than 50 percent.

Organics at relatively high concentrations produce significant spectral interferences on the photographic plate that make quantitation of the elements difficult. The tolerable level of organics has been estimated experimentally by McGregor et al. (1985) using coal and fly ash. Levels J50 percent as carbon tend to interfere significantly.

Solids or liquids containing high (J50 percent) levels of organics generally are subjected to dissolution in a pressurized Parr acid (HNO_3) bomb. The resulting aqueous solution then is slurried with the graphite electrode material, the water evaporated, and the electrode-sample mixture analyzed by SSMS. Samples that are aqueous to begin with are treated similarly. Fusions are not required in SSMS because their objective is to free up an element or elements of interest from a refractory matrix that would otherwise not dissolve. A key advantage of SSMS over plasma techniques and other methods that require samples to be liquid, is that inorganic samples need not be dissolved.

Figure 6-1 depicts the types of sample preparation procedures used for various environmental matrices.

6.3 SAMPLE INTRODUCTION TECHNIQUES

The most common sample introduction approach in SSMS is RF sparking of conducting electrodes containing the sample of interest. Electrodes generally are prepared using spectroscopic quality graphite, but 99.999-percent pure aluminum powder has been proposed as an alternative (Ure and Bacon 1976). Because most environmental materials are nonconducting, blending with a conducting material is required. To ensure that adequate results are obtained, the sample must be distributed homogeneously within the electrode matrix. This requires that solid samples be ground finely prior to mixing and that liquid samples be well mixed with the matrix in a slurry, taken to dryness, and mixed again.

The electrode sample mixture is formed into electrodes by a hydraulic press. Typically, they are clamped into the ion source with indium or tantalum holders. The sample-introduction and data-quality requirements of spark source are (1) the electrodes must be electrically conducting, (2) the physical strength must be sufficient to tolerate being clamped into the electrode holders, (3) there must be minimal interference from the mass spectrum of the support material, (4) any materials in the support material must be present at low, known concentrations, and (5) the contribution of the support material and sample to the spark and total ion current must be constant and consistent.

The electrodes are affixed into their holders in the source, which is then evacuated to around 10 to 7 torr. The electrodes are presparked against one another to remove surface contamination before the data-collection process begins.

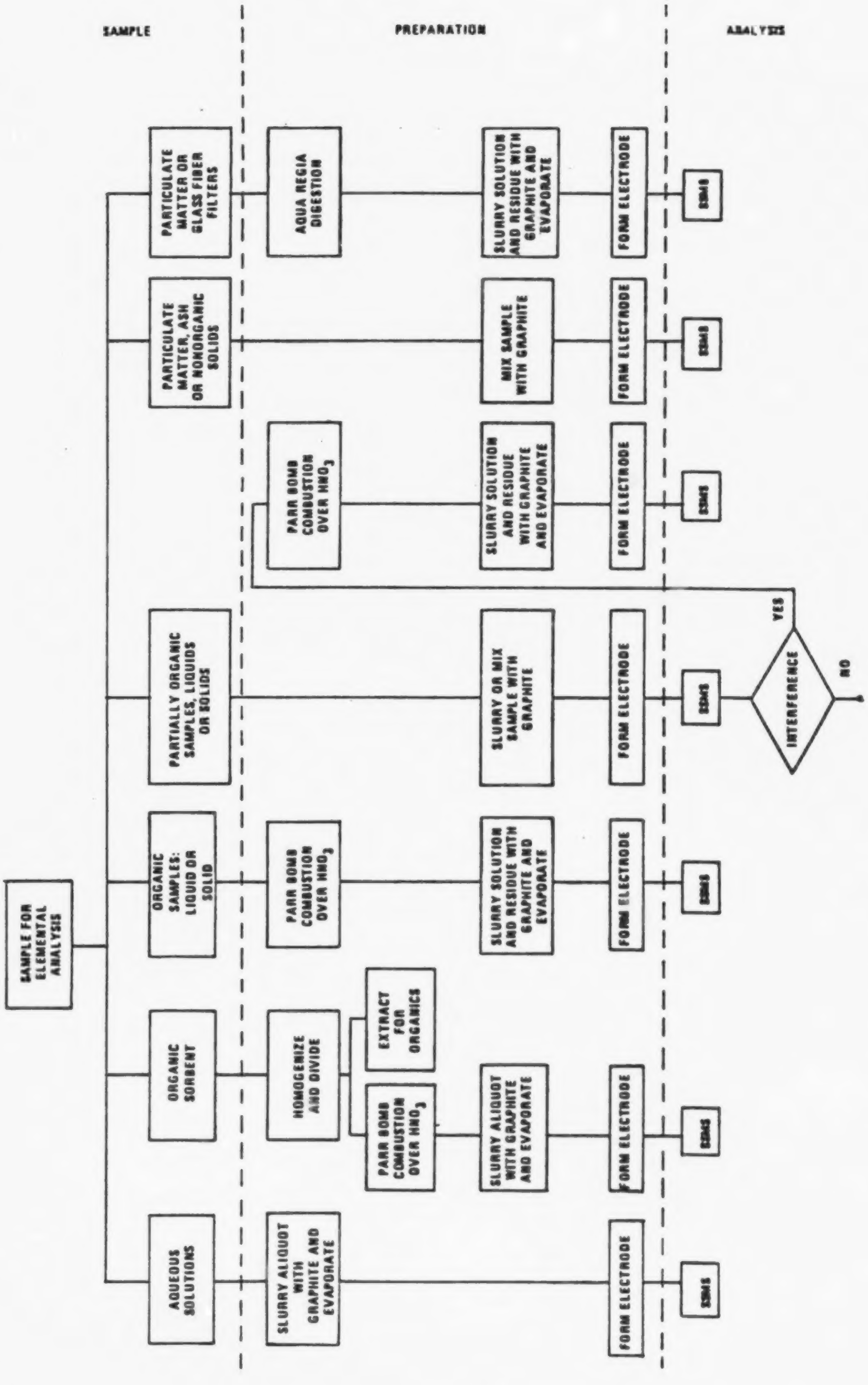
SAMPLE
PREPARATION
ANALYSIS
SAMPLE FOR ELEMENTAL ANALYSIS
AQUEOUS SOLUTIONS
ORGANIC SORBENT
ORGANIC SAMPLES: LIQUID OR SOLID
PARTIALLY ORGANIC SAMPLES, LIQUIDS OR SOLIDS
PARTICULATE MATTER, ASH OR NONORGANIC SOLIDS
PARTICULATE MATTER OR GLASS FIBER FILTERS
SLURRY ALIQUOT WITH GRAPHITE AND EVAPORATE
HOMOGENIZE AND DIVIDE
PARR BOMB COMBUSTION OVER HNO3
EXTRACT FOR ORGANICS
PARR BOMB COMBUSTION OVER HNO3
PARR BOMB COMBUSTION OVER HNO3
AQUA REGIA DIGESTION
SLURRY ALIQUOT WITH GRAPHITE AND EVAPORATE
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
SLURRY OR MIX SAMPLE WITH GRAPHITE
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
MIX SAMPLE WITH GRAPHITE
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
FORM ELECTRODE
SSMS
INTERFERENCE
YES
NO

Figure 6-1. Sample preparation for SSMS elemental analysis (Lentzen et al., 1978).

6.4 ELEMENT IDENTIFICATION AND QUANTITATION

6.4.1 Analysis Procedures and Detection Systems

There are two types of detection systems employed in SSMS. Photoplate detection, the most commonly used, is suitable for obtaining survey-type data for all elements heavier than lithium. Electrical detection, while considered more accurate than photoplate detection, is not suitable for determining more than a few elements at one time and will not be discussed further.

The electrodes are sparked by applying of an RF potential of around 4 kV, which generates an electrical discharge mainly composed of elemental and some molecular species. These are accelerated by an electrical field of 20 to 30 kV, which is energy-focused and momentum-dispersed. The ions are impacted onto an ion-sensitive photographic emulsion on a photoplate. The photoplate is subjected to a series of up to 16 graded exposures by varying the amount of ion charge allowed to reach the photoplate. The photoplates then are removed from the mass spectrometer and developed.

Quantitation is accomplished either by visual comparison of line intensities of an element of known concentration doped into the electrode as an internal standard to those of an element of interest or by measurement of line intensities using a microdensitometer. The visual method is the one most frequently employed in SSMS survey analysis. It involves determining the relative exposure of the spectral lines of each barely detectable element and those of the internal standard. Concentrations of elements of interest are then calculated using the relationship

$$C_u = C_k \cdot E_R \cdot A_R \cdot W_R \cdot M_R/S_R$$

where

C_u = the unknown concentration

C_k = the concentration of the internal standard

E_R = the ratio of the exposure required to yield the same spectral intensities for both the known and unknown elements

A_R = the ratio of the fractional abundances of the isotopes used for the determination

W_R = is the ratio of the relative widths of the spectral lines

M_R = the ratio of the photoplate response to the known and unknown isotope masses

S_R = the instrumental sensitivity of the unkown relative to the known. S_R is determined for a particular instrument generally by analyzing mixtures of elements of known composition in graphite.

6.4.2 Data Processing

As noted earlier, photoplates may be interpreted visually or by a microdensitometer that records line intensities. With either detection system the most frequently used approach is manually recording the data on standard forms and calculating the data reduction by entering data for the recorded variables into a computer program for data reduction. The analysis report consists of a presentation of concentrations calculated for each element identified in the sample.

6.5 ELEMENTAL COVERAGE

One of the outstanding advantages offered by SSMS is its reported comprehensive coverage of the periodic table. Elements from Li through U can be determined using photoplate detection. Depending on the source quoted, this coverage can exceed 70 elements in a single analysis of one sample. In this section, the documented capability of SSMS to determine specific categories of elements will be evaluated as will the overall capability of SSMS to carry out a qualitative, semiquantitative, and quantitative survey analysis of a sample.

6.5.1 Determination of Radioactive Elements

The 22 radioactive elements can be divided into the actinide series (all elements heavier than and including actinium) and all other elements known to be naturally radioactive.

Most of these elements exist in very small quantities in the environment and several only have been produced synthetically in the laboratory. For example, no weighable quantity of the element francium has ever been prepared or isolated, and the total amount of astatine present in the Earth's crust is less than 1 oz. Similarly, the elements from californium through lawrencium only have been produced in the laboratory and even then only in nanogram quantities. Most of the other actinide and radioactive elements exist only in areas contaminated with emissions from nearby nuclear weapons testings or as a result of emissions from the nuclear fuel cycle. Thus, it is not unexpected that all but a few of these elements are considered to be nondetectable by SSMS and other chemical analytical methods that measure the quantity of an element present. Methods that can measure the type of radiation emitted by these elements are sensitive enough to detect their presence, but are not considered in this comparison.

Uranium, thorium, radium, and radon occur naturally throughout the Earth's crust in rocks, soil, and some fossil energy deposits. No example of the determination of radium by SSMS could be found. The determination of radon, a gas, suffers from the same problems as other nonradioactive gases. The determination of gases is given in Section 5.7.2. No examples of its determination by SSMS could be found. Thorium and uranium have been determined routinely by SSMS in environmental samples.

While no environmental applications of SSMS to any other radioactive actinide elements could be found, it is important to note that SSMS is capable of making their determination, as shown in their determination as impurities in irradiated metals, liquids, and fuels that are used in the nuclear industry. Carter and Sites (1972) reported the determination of technetium in a chromium alloy and protactinium and promethium in fission products. They also reported the determination of relative sensitivity factors for U, Th, Np, Pu, Am, Cm, Bk, and Cf. They were calculated vs Er and ranged from 1.6 to 2.6 for a 1-mg sample. No application of SSMS was found for Po, At, Rn, Fr, Ra, Ac, Es, Fm, Md, No, and Lw.

The safety problems incumbent in the analysis of radioactive elements by SSMS deserve special attention (Carter and Sites 1972). Both the sample and the source must be enclosed in a glove box to contain the radioactivity. Nearly 99 percent of the radioactivity released during the sparking of a sample remains in the source. Less than 0.01 percent of the radioactivity is deposited on the photoplate. The source eventually will become contaminated and will require decontamination and replacement. Sample preparation safety measures for handling radioactive samples are also required.

These very sparse data indicate that very few environmental determinations of actinides and other radioactive elements have been conducted using SSMS (Table 6-1). While most of these elements should not be expected in most environmental samples, SSMS offers the capability to identify them as well as to identify other elements not normally radioactive but produced by nuclear processes. For example, Sr-90 and Cs-137, produced from the fission of uranium, could be distinguished from their nonradioactive isotopes in a sample, providing evidence that such contamination has occurred.

6.5.2 Determination of Nonmetals and Gases

In this study, 16 elements are considered to be nonmetals and gases. Because of the special sample preparation considerations in determining gases by SSMS, they will be discussed first.

The group of elements considered as gases are H, He, C, N, O, Ne, Ar, Kr, Xe, and Rn. Clearly, C is not a gas, but because it is usually included in any such determination, it will be discussed here.

Radon has been mentioned briefly in connection with other radioactive elements. The discussion of gases will be understood to include radon. Whereas information may be obtained on the distribution and mobility of these gases in samples under various conditions, this discussion will be limited to those analyses that determine the total quantity of gaseous element present.

Roboz (1972) discussed the determination of gases in solids by SSMS. Because any liquid sample would have to be evaporated onto or within an electrode matrix prior to sparking, this discussion can be extended to include liquid samples. Regardless of the original matrix, the electrode that is sparked probably will contain gases in one or more of the following forms:

- Gaseous elements in solid solution

TABLE 6-1. DOCUMENTED MULTIELEMENT COVERAGE CAPABILITY OF SSMS FOR NATURALLY RADIOACTIVE ELEMENTS

Element	Qualitative	Quantitative	Unacceptable or unknown
Astatine			X
Francium			X
Technetium		X	
Polonium			X
Promethium		X	
Radon			X
Radium			X
Actinium			X
Thorium		X	
Proctactinium		X	
Uranium		X	
Neptunium	X		
Plutonium	X		
Americium	X		
Curium	X		
Berkelium	X		
Californium	X		
Einsteinium			X
Fermium			X
Mendellurium			X
Nobelium			X
Laurencium			X

- Inclusions of a second phase as a hydride, nitride, or oxide
- Molecular gases in bubbles or crevices trapped during or prior to electrode solidification
- Adsorbed gases on surfaces.

While the SSMS technique offers the capability to identify each of these elements on the photoplate, its usefulness is greatly reduced due to its inability to distinguish elements of the first three forms from those introduced into the electrode during electrode preparation and those adsorbed on the electrode surface. The presence of the last two forms of contamination generally biases all subsequent attempts at element determination by SSMS. Because it is assumed, perhaps incorrectly, that most of the contamination will come from gases adsorbed onto the electrode surface, the standard procedure for reducing their contribution is to maintain the source pressure as low as possible via cryosorptive pumping to achieve a pressure of 1×10^{-8} torr and sub-ppm levels of H, N, C, and O. Some (Leipziger and Guidoboni 1967) have found that etching the electrodes with a non-oxygen-containing acid (HF or HCl) followed by baking the source overnight at 175 °C prior to analysis is necessary to reduce the adsorbed and source gas levels. Otherwise, the plates may indicate levels of 0.1 to 1 percent. The exposures also were made in reverse of the typical order, longest to shortest, to keep the sparking area free of readsorbed gases.

While such etching procedures are acceptable when analyzing metal electrodes, as in the case of the determination of inpurities in alloys, acids could not be used on the graphite electrodes that commonly are used to prepare environmental samples, because the electrodes would probably disintegrate. However, because Ure and Bacon (1976) demonstrate that environmental samples can be prepared in aluminum-based electrodes, it should be possible to determine the gaseous element content of environmental samples.

The other major problem with determining gaseous elements in environmental and other samples is that of interferences (Roboz 1972). Doubly charged $^{28}Si^{2+}$ interferes with the identification of $^{14}N^{+}$. Doubly charged $^{24}Mg^{2+}$ and $^{32}S^{2+}$ interfere with carbon ($^{12}C^{+}$ and $^{13}C^{+}$ lines) and oxygen, respectively. In environmental samples that frequently contain percentage levels of silicon, nitrogen determination would appear to be almost hopeless. $^{40}Ca^+$ interferes with $^{40}Ar^+$, effectively preventing its determination in environmental samples. Knowledge of the helium content of metals used in nuclear reactors is considered important; however, resolution of the $^4He^+$ line from $^{12}C^{3+}$ and $^{16}O^{4+}$ lines requires a resolution of >5,000 which may not be achievable on some instruments. The use of alternate isotope lines also does not help in cases of interference due to the low abundances of the naturally occurring stable isotopes of N, O, and C. All are below 1 percent of the main isotope. No discussion of the determination of Ne, Kr, and Xe could be found.

With the blank and interference problems that must be overcome, the applications of SSMS to gaseous element determination mainly have been restricted to metals and alloys. Typical examples of this use are shown in Table 6-2 where several NBS steels were analyzed for O and N content, and in Table 6-3 where several refractory metals were analyzed for hydrogen. Roboz (1972) reports that lunar samples were analyzed for oxygen content (41 percent) by SSMS, and ultrapure graphite for nitrogen and oxygen as low as 0.006 ppm.

It must be concluded that SSMS is a poor method for determining gaseous elements and carbon in environmental samples because of the blank and interference problems. The use of nongraphite electrode matrix material may improve the capability of the method, but this has yet to be demonstrated.

Coverage capability for nonmetals and gases is summarized in Table 6-4.

6.5.3 Determination of Noble or Precious Metals

All noble or precious metals have been determined quantitatively by SSMS.

6.5.4 Determination of Volatile or Hydride-Forming Elements

These elements also have been determined quantitatively (Conzemius et al. 1984).

6.5.5 Determination of Rare Earths and Lanthanides

All of these elements have been determined as part of general survey analyses (Conzemius et al. 1984) or separately as a group of elements in rocks and soils (Ure and Bacon 1976).

TABLE 6-2. ANALYSIS OF NBS STEELS FOR OXYGEN AND NITROGEN BY SSMS

	Oxygen (ppm)				Nitrogen (ppm)			
Sample	Expected	Found	Percent bias	Percent RSD[a]	Expected	Found	Percent bias	Percent RSD[a]
1041	170	130	-24	34	40	21	-48	19
1042	170	190	-12	35	140	93	-34	24
1044	90	70	-22	26	40	21	-48	31
1045	70	112	+60	44	40	54	-35	31

[a] Three determinations.

Source: Leipziger and Guidoboni, 1967.

TABLE 6-3. ANALYSIS OF REFRACTORY METALS FOR HYDROGEN (ppm)

Material	Expected	Found	% Bias
Molybdenum	1.0	0.7	-30
Niobium	2.0	1.8	-10
Tantalum	26	40	+54
Tungsten	0.9	1.8	+100

TABLE 6-4. DOCUMENTED MULTIELEMENT COVERAGE CAPABILITY OF SSMS FOR NONMETALS AND GASES IN ENVIRONMENTAL SAMPLES

Element	Qualitative	Quantitative	Unacceptable or unknown
Hydrogen		X	
Helium			X
Neon			X
Argon			X
Krypton			X
Xenon			X
Oxygen		X	
Carbon			
Nitrogen			X
Bromine		X	
Iodine		X	
Boron		X	
Fluorine		X	
Phosphorous		X	
Sulfur		X	
Chlorine		X	

6.5.6 Determination of Alkali and Alkaline Earth Metals

All of these elements have been determined as part of general survey analyses (Conzemius et al. 1984; and McGrath et al. 1984).

6.5.7 Determination of Transition Metals and Other Elements

All of these elements have been determined as part of general survey analyses (Conzemius et al. 1984; and McGrath et al. 1984).

6.6 DATA QUALITY

6.6.1 Detection Limits

Detection limits for SSMS analyses generally are on the order of 0.1 μg/g based on the original sample (Lentzen et al. 1978).

6.6.2 Precision

The precision of an SSMS analysis is limited by the variations in the ion currents produced by the RF spark. To smooth out these variations, beam choppers and automatic sparking devices have been employed. The use of the photoplate as a detector, with the difference between exposures on the order of a factor of two or three, also limits the precision. In general, precisions of around 50- to 100-percent RSD for repeat analyses of the same sample material are common for a survey analysis with photoplate detection and visual quantitation using the disappearing-line method (McGrath et al. 1984).

6.6.3 Accuracy

The accuracy of an SSMS analysis also is dependent on the factors that contribute to precision. Not surprisingly, the accuracy of SSMS analyses over a wide range of elements and concentrations also approaches 50 to 100 percent.

6.7 STANDARD OPERATING PROCEDURES

The only SSMS protocols that could be identified are those presented in IERL-RTP Procedures Manual for Level 1 Environmental Assessment (Lentzen et al. 1978), and in the EACS CS Manual (1979). These protocols are designed to provide data for more than 70 elements in one analysis of a sample. An instrumental resolution of 3,000 in the Pb+ ion region is required. The use of a photoplate ion-detection system is recommended. Electrode preparation is described for liquid and solid, organic and inorganic sample types. The general procedure calls for mixing 50 mg of ultrapure graphite and an internal quantitation standard with 1 to 20 mL of sample for liquids or 50 mg of sample for solids to form several electrodes for sparking. Erbium, indium, or rhenium are used as internal standards. Relative sensitivity coefficients are determined by analysis of a mixture of elements including the internal standard. Samples are analyzed in a like manner by the just-disappearing-line technique over a series of 15 exposures beginning at 300 nC and decreasing by a factor of 3 or 2. Procedures are given for calculating concentrations in the sample based on the photoplate responses. Examples of completed data forms are included. Procedures to assess data quality on a daily basis are described poorly. Method validation data are not provided.

SECTION 7

COMPARISON OF THE TECHNIQUES

7.1 EASE OF SAMPLE PREPARATION AND INTRODUCTION

The discussion and examples given in Sections 4, 5, and 6 demonstrate that the ICP-AES and SSMS techniques generally will require a vastly different set of sample preparation and introduction methods that depend primarily on the type matrix and, to a certain extent, on the element(s) of interest. Because both techniques can require sample preconcentration for certain elements to be detected and quantified, this discussion presumes that equal concentrations of all elements are present in all sample types at levels well above the detection limits of both techniques. Given these prerequisites, the issue is to decide in general which technique is better.

The SSMS technique is superior to the ICP-AES, with regard to sample preparation and introduction, for inorganic powders and other solid materials with less than 50-percent organic content amenable to grinding and fabrication of homogeneous electrodes. Thus, most geological type samples such as coal, soil, silicate rocks, fly ash, air particulates, and stream sediments will be transported more easily from the raw sample to the detector system in SSMS than in ICP-AES. Samples that are primarily organic in composition such as plant materials, other biota, animal tissue, oils, other liquid fuels, and aqueous samples in general are better suited to sample preparation and introduction into the ICP-AES.

7.2 ELEMENTAL COVERAGE, DATA QUALITY, AND THE ROLE OF EACH TECHNIQUE IN ENVIRONMENTAL ANALYSIS

The data presented in this study suggest that neither SSMS nor ICP-AES entirely is suitable for the comprehensive, precise, and accurate determination of all elements in all types of matrices and at all levels: there is no single technique that offers this capability. When appropriate steps to increase the elements present at below-instrumental detection limits and to permit the introduction of elements present in matrices incompatible with the instrument sample introduction/excitation systems are included, the total number of elements that can be determined by each technique can be extended to a maximum of around 100 elements. However, this cannot take place in a single sample or without putting forth an unacceptable amount of effort for the return that is expected.

The accuracy and precision of SSMS is much poorer than for ICP-AES even when comparing the analyses for matrices that easily are compatible with the SSMS. To achieve better accuracy and precision with SSMS, the number of elements to be determined would have to be reduced to only a handful.

The most significant conclusion to be made from this study is that SSMS and ICP-AES are complementary techniques that together provide a much greater coverage and detection capability than either technique alone when many different matrices are considered.

7.3 STANDARD OPERATING PROCEDURES

The applicability of any measurement technique to routine environmental analyses is dependent on the availability to users of documented protocols. Ideally, the protocols should be validated prior to dissemination for general use and should be compatible with commercially available instrumentation. Several recommended and required test methods for SSMS and plasma techniques have been prepared by the ASTM and the EPA in the last 7 years. Some of these protocols are quite detailed and almost can serve as "stand-alone" documents for analysis of certain types of samples. Others are, at best, guidelines for conducting analyses by these techniques and presume considerable prior knowledge on the part of the analyst.

Additional guidance is available in the operating and applications handbooks that accompany the instrumentation and in the open literature. However, with the exception of the EPA ICP-AES method for water and wastes, Method 200.7 (Federal Register 1984), there are no satisfactory comprehensive Standard Operating Procedures (SOPs) for SSMS or plasma techniques. The EPA method only is directly applicable to dilute aqueous samples and thus does not address the analysis of solids or nonaqueous liquids. Until such comprehensive SOPs are available, analysts will have to depend on the open literature and their own specific needs to develop methods of analysis for these type samples.

SECTION 8

PLASMA SOURCE MASS SPECTROMETRY--A MARRIAGE OF THE PLASMA AND THE MASS SPECTROMETER

8.1 BACKGROUND

One of the major limitations of SSMS is the unstable signal produced from the RF sparking of sample constituents and matrix from the electrode surface. This results in poor precision and generally limits the method's usefulness in quantitative analysis. One of the major disadvantages of plasma spectroscopy is the time consuming and often unsatisfactory effort that must be made to identify and correct for spectral interferences.

On the other hand, the mass spectrometer detector system used in SSMS provides for elemental coverage over nearly the entire periodic table. Likewise, the ICP is, in principle, an excellent source for mass spectrometry, because most elements are highly ionized as monovalent, positive ions. If these two strengths of these techniques could be combined, a powerful new analytical technique would be the result. Research along this line of thought resulted in the development of the hybrid technique inductively coupled plasma-mass spectrometry (ICP-MS) in which the sample is converted into ions in the plasma and the positive atomic ions are separated according to their mass in a mass spectrometer and detected by an electron multiplier. Houk et al. (1980) described the basic theory behind ICP-MS, and Date and Gray (1983) and Douglas and Houk (1984) covered recent progress. The first commercially available ICP-MS systems were produced by VG Instruments (The VG Plasma Quad Spectrometer) and SCIEX (the ELAN 250 Elemental Analyzer) in 1983. The operating principles of ICP-MS and what is known of commercial instrumentation and applications are discussed herein.

8.2 OPERATING PRINCIPLES

Liquid aqueous samples are aerosolized by a cross-flow or concentric pneumatic nebulizer and are injected into a horizontally mounted inductively coupled argon plasma source. Hydride generation and electrothermal atomization systems can be interfaced with the plasma if desired. The ICP heats the sample to approximately 7,000 K so that the dissolved solids are vaporized, atomized, and ionized. Up to this point, the sample has experienced conditions identical to those in ICP-AES. However, instead of being detected by a grating spectrophotometer-photomultiplier tube system, a small fraction of the sample ions produced by the plasma are drawn through a water-cooled sampling orifice maintained at approximately 1 torr and are transmitted by a lens system into a quadrupole mass spectrometer. Ion currents generated by the positive sample ions are recorded and presented as a mass spectrum much as in SSMS. Each ion that is detected is recorded as one "count" and the counts observed at a particular atomic mass unit (amu) are presented in counts per second (c/s). The spectra are much simpler than those produced in SSMS and primarily consist of singly charged monoatomic elemental ions (M^+) or simple oxide ions (MO^+).

The ICP-MS instrument marketed by SCIEX, the ELAN 250 ICP-MS (SCIEX Product Note--Instrument Description), can determine 1 element/second at levels >10 × detection limit; near the detection limit, 1 element/10 seconds. Rapid semiquantitative analysis is possible, but how rapidly and the extent of elemental coverage is not stated. The time required for steady-state response to a blank after analysis of a sample is about 1 min and is a function of the nebulizer/spray chamber arrangement of the ICP system (Douglas et al. 1983).

In the VG Plasma Quad system, a new sample can be aspirated every 2 min after termination of the previous sample's aspiration. Data are acquired by a high-gain single-channel electron multiplier, which is said to provide a linear response over six orders of magnitude. The entire spectrum that is generated can be stored and reproduced for later interpretation. This is a feature of both instruments.

8.3 ICP-MS INTERFACE

Because the ICP operates at atmospheric pressure and 7,000 K and the mass spectrometer at pressures less than 10^{-5} torr at 300 K, a suitable interface is needed so that stable, reproducible extraction of ions from the plasma can be achieved without cooling or distorting the plasma (Douglas and Houk 1984).

Date and Gray (1983) described two sampling modes in which ion samples are transmitted from the plasma into the vacuum system of the mass spectrometer. In the boundary layer sampling mode, ions extracted from the tail flame of the ICP pass through a boundary layer of cool gas that forms over the sampling orifice. Although high signal-to-background ratios and low (sub µg/L) detection limits are achievable, this sampling mode will not tolerate solutions with greater than 10 mg/L total dissolved solids. The small diameter of the sampling orifice is subject to clogging with dissolved salts, to melting, or to erosion during use resulting in a higher background spectrum than is considered acceptable. To overcome this limitation and to extend the usefulness of the method to more complex samples, a second sampling mode, continuum sampling, is used. In this method the tail of the plasma discharge is pinched by increasing the mass spectrometer sampling orifice diameter, resulting in a controlled expansion of the plasma gas into the vacuum system. The continuum sampling mode is the one used in commercially available instrumentation. The principal disadvantage of continuum vs. boundary-layer sampling is somewhat higher detection limits (Table 8-1), but this is offset by the increased ruggedness of the orifice and its ability to handle much higher salt concentrations before plugging, even when solutions as great as 5,000 mg/L are analyzed (Douglas et al. 1983), although other data suggests that the upper limit is 1,000 mg/L (0.1 percent).

8.4 OPERATING RANGE AND DETECTION LIMITS

Detection limits in ICP-MS are generally an order of magnitude lower than those in ICP-AES. Detection limits obtained using the continuum sampling mode are 0.1 to 1 µg/L for a broad range of elements. As an example, in Table 8-2 single element detection limits are compared for rare earths.

Reported detection limits typically are obtained in single-element solutions but may be nearly the same in multielement mixtures or complex matrices unless there are interferences or matrix effects, although this has yet to be demonstrated. For example, the ICP-MS orifice cannot tolerate total salt levels of >0.1 percent, therefore dilution of all samples to below this level is required and may result in increased detection limits for certain elements.

TABLE 8-1. DETECTION LIMITS (3σ, µg/L) IN PLASMA SOURCE MASS SPECTROMETRY

Element	Ion	Boundary layer mode	Ion	Continuum mode
Lithium	$^{7}Li^{+}$	0.4	--	5.0
Boron	--	--	$^{11}B^{+}$	2.0
Magnesium	$^{24}Mg^{+}$	0.2	--	0.7
Aluminum	$^{27}Al^{+}$	0.3	--	0.9
Titanium	--	--	$^{48}Ti^{+}$	0.5
Vanadium	$^{67}VO^{+}$	0.3	$^{51}V^{+}$	0.6
Chromium	$^{52}Cr^{+}$	0.1	--	0.2
Manganese	$^{55}Mn^{+}$	0.06	--	1.3
Iron	$^{56}Fe^{+}$	0.5	--	--
Cobalt	$^{59}Co^{+}$	0.1	--	0.8
Copper	$^{63}Cu^{+}$	0.3	--	--
Zinc	$^{64}Zn^{+}$	2.0	$^{66}Zn^{+}$	4.3
Germanium	--	--	$^{72}Ge^{+}$	1.6
Arsenic	$^{75}As^{+}$	0.1[a]	--	11
Selenium	--	--	$^{78}Se^{+}$	23
Rubidium	$^{85}Rb^{+}$	0.2	--	0.4
Silver	$^{107}Ag^{+}$	0.1	--	0.3
Cadmium	$^{114}Cd^{+}$	0.2	--	0.7
Indium	--	--	$^{115}In^{+}$	0.2
Tellurium	--	--	$^{130}Te^{+}$	0.7
Cesium	--	--	$^{133}Cs^{+}$	0.2
Barium	$^{138}Ba^{+}$	0.2	$^{138}Ba^{2+}$	0.4
Lanthanum	--	--	$^{139}La^{+}$	3.4
	--	--	$^{139}La^{2+}$	0.3
Cerium	--	--	$^{140}Ce^{+}$	1.5
Tungsten	--	--	$^{184}W^{+}$	0.7
Gold	--	--	$^{197}Au^{+}$	0.2
Mercury	$^{202}Hg^{+}$	2.0		0.6
Lead	$^{208}Pb^{+}$	0.2		0.4
Bismuth	--	--	$^{209}Bi^{+}$	0.3
Thorium	--	--	$^{232}Th^{+}$	1.5
			$^{232}Th^{2+}$	0.3
Uranium	$^{270}UO_2^{+}$	0.05	$^{238}U^{+}$	0.5
			$^{238}U^{2+}$	0.5

[a] Hydride generation.

Source: Date and Gray (1983)

TABLE 8-2. COMPARISON OF ICP-MS AND ICP-AES DETECTION LIMITS

Element	μg/L ICP-MS[a]	μg/L ICP-AES[b,c]
Y	0.3	2.7
Yb	0.9	3.3
Gd	2.0	27
Ce	1.0	46
Ho	0.4	5.4
Sc	3.2	Not given

[a] 3σ, 10-s measurement time.

[b] 3σ, 30-s measurement time.

[c] F. Lichte, Anal. Chem. 54, 1329, 1982 detection limits converted from S/N = 2 (2σ) to SN = 3 (3σ) values.

Notes:

1. Detection limits are defined for 10-s counting period and will degrade as $(\sqrt{\text{measurement time}})^{-1}$

2. Nebulizer was Meinhard type (25 psi, uptake rate = 1.7 mL min^{-1})

3. Background noise is less than 20 cps at all masses.

4. Detection limits obtained using the continuum sampling mode are 0.1 to 1 μg/L for a broad range of elements.

Very low detection limits are given in the marketing literature for the VG Instruments Plasma Quad ICP-MS (Table 8-3). These are based on analysis of aqueous standards at 1 to 4 mL/min using 10-s integrations with the mass spectrometer optimized for each element. It is stated that determination of more than one element at a time will require "compromise conditions" with probable increases in detection limits of a factor of 2 or 3. Somewhat higher detection limits are given for the SCIEX ELAN ICP-MS (Table 8-4).

The upper limit of the ICP-MS operating range is 1 to 10 mg/L. Based on a 0.1 µg/L detection limit, this range covers five orders of magnitude, although this range has not been demonstrated for multielement mixtures. The operating range of ICP-MS is therefore considerably lower than that of ICP-AES and SSMS and will require sample dilution if major elements are to be determined. This will prevent the simultaneous determination of many elements in a single sample, because a broad range of concentrations typically is encountered in environmental samples. It is unlikely that the comprehensive elemental coverage capability of this technique can be demonstrated on environmental samples for this reason, although determination of 40 or more elements may be possible.

8.5 INTERFERENCES AND MATRIX EFFECTS

According to Douglas and Houk (1984), spectral interferences in ICP-MS can arise from background peaks, isobaric singly charged ions from different elements than the one expected at a given mass unit, doubly charged ions, oxide ions, and other molecular ions.

Spectral background is not considered to be a significant interference. By comparison there are only 211 lines to consider for all elements in ICP-MS whereas there are thousands of lines to consider in ICP-AES. Although a noise level of 1 to 20 c/s is observed across the entire mass range, 2 to 300 amu (Douglas et al. 1983; Douglas and Houk 1984), the most significant background peaks occur below 42 amu. These are due to argon (Ar^+ at 40 amu) and H_3O^+ ions from water or from dissolved and entrained air.

TABLE 8-3. DETECTION LIMITS FOR PLASMA QUAD ICP-MS[a]

Element	Detection limit (μg/L)
Li	0.06
B	0.2
Be	0.04
Co	0.03
Zn	0.7
Ge	0.02
As	0.02
Se	0.5
Ag	0.02
Cd	0.04
Sn	0.05
Au	0.04
Hg	0.01
Pb	0.03
Th	0.06
U	0.06

Note: Examples of detection limits from nebulized dilute aqueous solutions. Detection limits are calculated as 2 σ values of background (blank).

[a] VG Instruments (1984).

TABLE 8-4. SCIEX DETECTION LIMITS, SINGLE ELEMENT, μg/L EITHER WITH 30 OR 100 INTEGRATION TIME

Element	μg/L	Element	μg/L	Element	μg/L
Li	2	Y	0.8	Pb	0.8
B	2	Zr	1	Bi	0.6
C	50	Nb	1	Ce	1
F	30,000	Mo	2	Pr	1
Na	2	Ru	4	Nd	2
Mg	1	Rh	1	Sm	2
Al	3	Pd	0.4	Eu	2
P	300	Ag	1	Gd	2
S	1,000	Cd	2	Tb	2
Sc	3	In	1	Dy	1
Ti	2	Sn	2	Ho	0.4
V	2	Te	0.4	Er	2
Cr	1	I	2	Tm	0.5
Mn	1	Cs	1	Y	0.9
Fe	4	Ba	1	Lu	1
Co	0.8	La	1	Th	0.7
Ni	2	W	2	U	1
Cu	1.5	Re	2		
Zn	2	Os	0.8		
As	50	Ir	2		
Se	80	Pt	1		
Br	100	Au	0.4		
Rb	0.8	Hg	1.3		
Sr	0.8	Tl	0.6		

No species higher than a doubly charged ion has been observed. Doubly charged ions are present only for a few elements at low levels (Douglas and Houk 1984). Oxide ions (MO^+) are seen for some refractory elements.

Molecular ions resulting from acids used in sample preparation can be a significant interference for certain elements. For example, perchloric and hydrochloric acids produce the ion ClO^+ at masses of 51 and 53, which interferes with 51_V^+. Likewise, ClO_2^+ at masses of 67 and 69 interferes with ^{67}Zn and ^{69}Ge. $ArCl^+$ at masses of 75 and 77 interferes with ^{75}As. The impact of nitric, sulfuric, and hydrofluoric acids on spectral interferences have not been described.

The ICP-MS system is somewhat more sensitive to suppression of target element signal levels in the presence of high levels of major elements. Douglas and Houk (1984) report that a 20-percent suppression of the signal for 10 mg/L Co and a 10-percent suppression for 10 mg/L Bi, Cu, and Zn is observed in the presence of 1,000 mg/L Na. In ICP-AES, 10-times greater levels of Na are required to produce a similar signal reduction. However, for other elements, major interferences that exist in ICP-AES are nonexistent in ICP-MS. A solution containing 50 µg/L Pd and Te in a 500 g/L Ca solution showed no interference due to Ca (SCIEX--Preliminary Product Note--Interferences).

Thus, while the ICP-MS does not suffer from the same types of spectral interferences associated with the ICP, it is clear that there are some interferences and most are a result of the requirement that samples be prepared so that they can be introduced into the ICP in the form of a dilute aqueous mixture.

8.6 APPLICATIONS

Although ICP-MS marketing and published literature generally states that more than 90 percent of the elements in the periodic table can be determined, relatively few applications have been described and none of these adequately demonstrate that this degree of coverage is achievable.

The cap[illegible] of the technique to determine adequately some nonmetals is questi[illegible]e. Single-element detection limits for the halogens are much higher [illegible]an for the majority of elements. Douglas and Quan (1983) have reported that carbon has been detected as C^+ ion at a detection limit in water of 50 µg/L as carbonate. They indicate that the use of negative ions will expand the coverage of elements, provided that this capability can be developed in ICP-MS.

One potential capability of ICP-MS, not available in ICP-AES but commonly employed in SSMS, is that of isotope dilution. By spiking a digested sample with an isotope of the element of interest and measuring the altered isotope ratio of the element, the element of interest can be quantitated with a high degree of accuracy and precision. This method has been used in SSMS to provide for highly accurate and precise measurements of elemental concentrations. Unfortunately, in SSMS only a few elements per sample can be quantitated by isotope dilution. Although it is claimed that rapid multielemental isotope dilution determinations are possible with ICP-MS (SCIEX IDMSS) no examples have been described. A single-element analysis of Cu in an NBS Orchard Leaves Digest is the only example presented.

Although the VG marketing literature states that

> "The VG Plasma Quad can determine [analyze] more elements in the periodic table than any other method, at lower concentrations (some at parts per trillion) and over a wider range of concentrations."

there is insufficient documentation provided by VG that this is indeed the case. Understandably, the data base for their system and for ICP-MS in general must be considered quite limited at the present time due to the newness of the technique. According to Mr. John Kendall of VG, only five units were delivered as of May, 1984. The VG literature does provide examples of possible applications of ICP-MS to the analysis of water samples, fly ash, biological matrices, and industrial alloys, but in no case is data for more than 25 elements in a single sample presented. However, the elements for which data are presented are among those that generally cannot be determined by SSMS, ICP-AES, or even AAS, e.g., Hg (20 µg/L), Pb (2 µg/L), I (1 µg/L), Br (100 µg/L), and Ba (50 µg/L) in tapwater; As, Ti, Th, and U in NBS SRM 1633 fly ash; Cd, I, Cs, Pb, Rb, Co, Sc, Cu, and Zn in blood; Cd and Bi in U; and La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Yb, and Lu in Co/Sm magnet alloy at levels from 4 to 400 mg/L. A mixture of 25 elements at 1 mg/L in water was presented showing the capability of the technique to determine in a clean matrix at relatively high levels Li, Be, B, Na Mg, Al, K, Cr, Mn, Fe, Ni, Co, Cu, Zn, Ga, Sr, Ag, Cd, In, Ba, Pt, Au, Tl, Pb, and Bi. Clearly ICP-MS has great potential for determining some nonmetals and REE's in environmental samples.

The cost of the instrumentation, estimated by Mr. Kendall of VG at $200,000, will be prohibitive for small laboratories and thus will restrict the market to government, academic, and private research laboratories performing geological, environmental, and related elemental characterization studies. Currently, no information is available on the cost per analysis of a sample.

SECTION 9

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